

WEST Search History

DATE: Saturday, May 03, 2003

<u>Set</u> <u>Name</u> side by side	<u>Query</u>	<u>Hit</u> <u>Count</u>	<u>Set Name</u> result set
<i>DB=USPT,PGPB; PLUR=YES; OP=OR</i>			
L14	L13 or l12 or l11	38	L14
L13	L4 and l6	34	L13
L12	L4 and l7	25	L12
L11	L10 and l4	19	L11
L10	L9 and l5	64	L10
L9	L8 and l6	133	L9
L8	L7 and (radical)	850	L8
L7	(spin near3 (trap\$6 or label\$5))	1722	L7
L6	nitron\$6	2731	L6
L5	PBN	907	L5
L4	L3 or l2 or l1	2656	L4
L3	((564/282)!.CCLS.)	309	L3
L2	((562/62)!.CCLS.)	34	L2
L1	((315,399,422,428,517,518,645,708,709/)!.CCLS. (514/400 514/654 514/644 514/641 514/619 514/643 514/226.2)!.CCLS.)	2344	L1

END OF SEARCH HISTORY

* * * * * STN Columbus * * * * *

FILE 'HOME' ENTERED AT 11:11:52 ON 03 MAY 2003

=> file reg

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'REGISTRY' ENTERED AT 11:12:06 ON 03 MAY 2003

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2003 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 2 MAY 2003 HIGHEST RN 509953-09-7

DICTIONARY FILE UPDATES: 2 MAY 2003 HIGHEST RN 509953-09-7

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2003

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNnote 27, Searching Properties in the CAS Registry File, for complete details:

<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> e 66893-81-0/cn

E1	1	6688: PN: WO9514772 SEQID: 6683 CLAIMED SEQUENCE/CN
E2	1	6689 PN: WO0118542 TABLE: 3A-1 CLAIMED DNA/CN
E3	0 -->	66893-81-0/CN
E4	1	6689: PN: EP1281758 SEQID: 6720 UNCLAIMED DNA/CN
E5	1	6689: PN: WO0078341 PAGE: 79 UNCLAIMED SEQUENCE/CN
E6	1	6689: PN: WO0153836 TABLE: 3-3 CLAIMED DNA/CN
E7	1	6689: PN: WO0164835 SEQID: 13689 CLAIMED DNA/CN
E8	1	6689: PN: WO0164835 SEQID: 20590 CLAIMED PROTEIN/CN
E9	1	6689: PN: WO0164835 SEQID: 27689 CLAIMED PROTEIN/CN
E10	1	6689: PN: WO0164835 SEQID: 6389 CLAIMED SEQUENCE/CN
E11	1	6689: PN: WO0177384 SEQID: 381689 CLAIMED DNA/CN
E12	1	6689: PN: WO9514772 SEQID: 6684 CLAIMED SEQUENCE/CN

=> e POBN/cn

E1	1	POBILUKAST/CN
E2	1	POBILUKAST EDAMINE HYDRATE/CN
E3	1 -->	POBN/CN
E4	1	POBO/CN
E5	1	POBR PROTEIN (BRUCELLA MELITENSIS BIOVAR SUIS STRAIN 1330 GENE POBR)/CN
E6	1	POBR REGULATOR (PSEUDOMONAS SP. STRAIN HR199(DSM-7063) GENE POBR)/CN
E7	1	POBR REGULATOR (XANTHOMONAS AXONOPODIS CITRI STRAIN 306 GENE POBR)/CN
E8	1	POBR REGULATOR (XANTHOMONAS CAMPESTRIS CAMPESTRIS STRAIN ATC C33913 GENE POBR)/CN
E9	1	POC 202/CN
E10	1	POC 2020/CN

E11 1 POC MEDIUM/CN
 E12 1 POC-AS 0010/CN

=> s e3

L1 1 POBN/CN

=> d l1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2003 ACS

RN 66893-81-0 REGISTRY

CN 2-Propanamine, 2-methyl-N-[(1-oxido-4-pyridinyl)methylene]-, N-oxide (9CI)
 (CA INDEX NAME)

OTHER CA INDEX NAMES:

CN 2-Propanamine, 2-methyl-N-(4-pyridinylmethylene)-, N,N'-dioxide

OTHER NAMES:

CN .alpha.-(4-Pyridyl-1-oxide)-N-tert-butyl nitron

CN 4-POBN

CN C-(4-Pyridinyl-N-oxide)-N-tert-butyl nitron

CN N-tert-Butyl-.alpha.-(4-pyridyl-1-oxide) nitron

CN **POBN**

FS 3D CONCORD

DR 83016-64-2

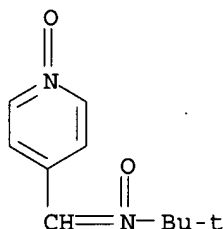
MF C10 H14 N2 O2

CI COM

LC STN Files: AGRICOLA, BEILSTEIN*, BIOSIS, CA, CAPLUS, CASREACT, CHEMCATS,
 CHEMLIST, CSCHEM, MSDS-OHS, NIOSHTIC, TOXCENTER, USPATFULL
 (*File contains numerically searchable property data)

Other Sources: EINECS**

(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

144 REFERENCES IN FILE CA (1957 TO DATE)

12 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA

143 REFERENCES IN FILE CAPLUS (1957 TO DATE)

=> e 66893-81-0/rn

E1 1 66893-79-6/RN
 E2 1 66893-80-9/RN
 E3 1 --> 66893-81-0/RN
 E4 1 66893-82-1/RN
 E5 1 66893-83-2/RN
 E6 1 66893-84-3/RN
 E7 1 66893-85-4/RN
 E8 1 66893-86-5/RN
 E9 1 66893-87-6/RN
 E10 1 66893-88-7/RN
 E11 1 66893-89-8/RN
 E12 1 66893-90-1/RN

=> s e3

L2 1 66893-81-0/RN

=> e 3376-24-7/rn

E1 1 3376-14-5/RN

E2 1 3376-23-6/RN

E3 1 --> 3376-24-7/RN

E4 1 3376-25-8/RN

E5 1 3376-26-9/RN

E6 1 3376-27-0/RN

E7 1 3376-29-2/RN

E8 1 3376-30-5/RN

E9 1 3376-32-7/RN

E10 1 3376-33-8/RN

E11 1 3376-34-9/RN

E12 1 3376-35-0/RN

=> s e3

L3 1 3376-24-7/RN

=> d l3

L3 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2003 ACS

RN 3376-24-7 REGISTRY

CN 2-Propanamine, 2-methyl-N-(phenylmethylene)-, N-oxide (9CI) (CA INDEX NAME)

OTHER CA INDEX NAMES:

CN Nitron, N-tert-butyl-.alpha.-phenyl- (6CI, 7CI, 8CI)

OTHER NAMES:

CN .alpha.-Phenyl-N-tert-butylnitron

CN .alpha.-Phenyl-tertbutyl nitron

CN 2-Methyl-N-(phenylmethylene)-2-propanamine N-oxide

CN 2-Phenyl-N-tert-butylnitron

CN Benzylidene-tert-butylamine N-oxide

CN Benzylidene-tert-butylamine oxide

CN C-Phenyl-N-tert-butylnitron

CN C-Phenyl-N-tert-butylnitron

CN N-Benzylidene-tert-butylamine N-oxide

CN N-Benzylidene-tert-butylamine oxide

CN N-tert-Butyl-.alpha.-phenylnitron

CN N-tert-Butyl-2-phenylnitron

CN N-tert-Butyl-C-phenylnitron

CN PBN

CN PBN (amine oxide)

CN tert-Butyl(benzylidene)amine N-oxide

FS 3D CONCORD

DR 165047-88-1, 173777-90-7, 50643-08-8, 68315-30-0, 154345-12-7, 115995-20-5

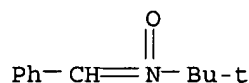
MF C11 H15 N O

CI COM

LC STN Files: AGRICOLA, BEILSTEIN*, BIOBUSINESS, BIOSIS, BIOTECHNO, CA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CHEMCATS, CHEMINFORMRX, CHEMLIST, CSCHEM, CSNB, DDFU, DETHERM*, DRUGU, EMBASE, IPA, MEDLINE, MRCK*, MSDS-OHS, NIOSHTIC, RTECS*, SPECINFO, TOXCENTER, USPAT2, USPATFULL (*File contains numerically searchable property data)

Other Sources: EINECS**, NDSL**, TSCA**

(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1011 REFERENCES IN FILE CA (1957 TO DATE)
24 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
1010 REFERENCES IN FILE CAPLUS (1957 TO DATE)
8 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=> e 3317-61-1/rn

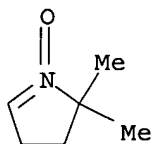
E1	1	3317-59-7/RN
E2	1	3317-60-0/RN
E3	1 -->	3317-61-1/RN
E4	1	3317-62-2/RN
E5	1	3317-63-3/RN
E6	1	3317-66-6/RN
E7	1	3317-67-7/RN
E8	1	3317-68-8/RN
E9	1	3317-72-4/RN
E10	1	3317-75-7/RN
E11	1	3317-77-9/RN
E12	1	3317-78-0/RN

=> s e3

L4 1 3317-61-1/RN

=> d 14

L4 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2003 ACS
RN 3317-61-1 REGISTRY
CN 2H-Pyrrole, 3,4-dihydro-2,2-dimethyl-, 1-oxide (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN 1-Pyrroline, 5,5-dimethyl-, 1-oxide (6CI, 7CI, 8CI)
OTHER NAMES:
CN 2,2-Dimethyl-3,4-dihydro-2H-pyrrole N-oxide
CN 5,5-Dimethyl-.DELTA.1-pyrroline 1-oxide
CN 5,5-Dimethyl-.DELTA.1-pyrroline N-oxide
CN 5,5-Dimethyl-1-pyrroline 1-oxide
CN 5,5-Dimethyl-1-pyrroline N-oxide
CN 5,5-Dimethyl-4,5-dihydro-3H-pyrrole N-oxide
CN DMPO
FS 3D CONCORD
MF C6 H11 N O
CI COM
LC STN Files: AGRICOLA, ANABSTR, BEILSTEIN*, BIOBUSINESS, BIOSIS,
BIOTECHNO, CA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CHEMCATS,
CHEMINFORMRX, CHEMLIST, CSCHEM, EMBASE, IFICDB, IFIPAT, IFIUDB, MEDLINE,
MRCK*, MSDS-OHS, PIRA, TOXCENTER, USPAT2, USPATFULL
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

825 REFERENCES IN FILE CA (1957 TO DATE)

46 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
826 REFERENCES IN FILE CAPLUS (1957 TO DATE)
7 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=> e 2564-83-2/rn

E1	1	2564-81-0/RN
E2	1	2564-82-1/RN
E3	1 -->	2564-83-2/RN
E4	1	2564-84-3/RN
E5	1	2564-86-5/RN
E6	1	2564-87-6/RN
E7	1	2564-88-7/RN
E8	1	2564-89-8/RN
E9	1	2564-92-3/RN
E10	1	2564-94-5/RN
E11	1	2564-95-6/RN
E12	1	25640-01-1/RN

=> s e3

L5 1 2564-83-2/RN

=> d 15

L5 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2003 ACS

RN 2564-83-2 REGISTRY

CN 1-Piperidinyloxy, 2,2,6,6-tetramethyl- (9CI) (CA INDEX NAME)

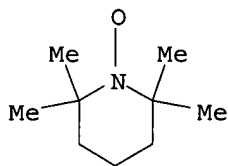
OTHER CA INDEX NAMES:

CN Piperidinoxy, 2,2,6,6-tetramethyl- (7CI, 8CI)

OTHER NAMES:

CN 1,1,5,5-Tetramethylpentamethylene nitroxide
CN 1-Oxyl-2,2,6,6-tetramethylpiperidine
CN 2,2,6,6-Tetramethyl-1-oxylpiperidine
CN 2,2,6,6-Tetramethyl-1-piperadoxyl
CN 2,2,6,6-Tetramethyl-1-piperidinoxyl
CN 2,2,6,6-Tetramethyl-1-piperidinyloxy
CN 2,2,6,6-Tetramethyl-1-piperidyloxy
CN 2,2,6,6-Tetramethylpiperidin-1-oxy
CN 2,2,6,6-Tetramethylpiperidin-1-oxyl radical
CN 2,2,6,6-Tetramethylpiperidin-N-oxyl
CN 2,2,6,6-Tetramethylpiperidine N-oxide
CN 2,2,6,6-Tetramethylpiperidine N-oxide radical
CN 2,2,6,6-Tetramethylpiperidine N-oxy
CN 2,2,6,6-Tetramethylpiperidine N-oxyl
CN 2,2,6,6-Tetramethylpiperidine N-oxyl radical
CN 2,2,6,6-Tetramethylpiperidine nitroxide
CN 2,2,6,6-Tetramethylpiperidine nitroxide radical
CN 2,2,6,6-Tetramethylpiperidine oxide
CN 2,2,6,6-Tetramethylpiperidine-1-oxyl
CN 2,2,6,6-Tetramethylpiperidino-1-oxy
CN 2,2,6,6-Tetramethylpiperidinoxy
CN 2,2,6,6-Tetramethylpiperidinoxy radical
CN 2,2,6,6-Tetramethylpiperidinoxyl
CN 2,2,6,6-Tetramethylpiperidinoxyl
CN 2,2,6,6-Tetramethylpiperidinoxyl radical
CN 2,2,6,6-Tetramethylpiperidinyl 1-oxide
CN 2,2,6,6-Tetramethylpiperidinyl-1-oxyl
CN 2,2,6,6-Tetramethylpiperidinyl-N-oxy
CN 2,2,6,6-Tetramethylpiperidinyloxy
CN 2,2,6,6-Tetramethylpiperidoxyl
CN HO 6
CN Tanan
CN Tanane
CN Tempo

CN TEMPO
 CN TMPO
 DR 126517-51-9, 54637-06-8, 125012-91-1, 64104-42-3, 25657-03-8, 26933-82-4
 MF C9 H18 N O
 CI COM
 LC STN Files: AGRICOLA, ANABSTR, BEILSTEIN*, BIOBUSINESS, BIOSIS, CA,
 CANCERLIT, CAOLD, CAPLUS, CASREACT, CEN, CHEMCATS, CHEMINFORMRX,
 CHEMLIST, CIN, CSCHM, DDFU, DRUGU, GMELIN*, IFICDB, IFIPAT, IFIUDB,
 IPA, MEDLINE, MRCK*, NIOSHTIC, PIRA, PROMT, RTECS*, TOXCENTER, USPAT2,
 USPATFULL
 (*File contains numerically searchable property data)
 Other Sources: EINECS**, TSCA**
 (**Enter CHEMLIST File for up-to-date regulatory information)



2371 REFERENCES IN FILE CA (1957 TO DATE)
 100 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
 2383 REFERENCES IN FILE CAPLUS (1957 TO DATE)
 23 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=>

=> FIL REGISTRY

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	13.34	13.55

FILE 'REGISTRY' ENTERED AT 11:15:40 ON 03 MAY 2003
 USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
 PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
 COPYRIGHT (C) 2003 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 2 MAY 2003 HIGHEST RN 509953-09-7
 DICTIONARY FILE UPDATES: 2 MAY 2003 HIGHEST RN 509953-09-7

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2003

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STN Note 27, Searching Properties in the CAS Registry File, for complete details:
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> SET TERMSET E#

SET COMMAND COMPLETED

=> DEL SEL Y

=> SEL L1 1 RN

E1 THROUGH E1 ASSIGNED

=> S E1/RN

L6 1 66893-81-0/RN

=> SET TERMSET LOGIN

SET COMMAND COMPLETED

=> FIL CHEMLIST

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.48	14.03

FILE 'CHEMLIST' ENTERED AT 11:15:45 ON 03 MAY 2003
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2003 American Chemical Society (ACS)

FILE COVERS 1979 TO 2 MAY 2003 (20030502/UP)

This file contains CAS Registry Numbers for easy and accurate substance identification.

TSCA Inventory Tape information is current through January 6, 2003 as provided by the January 2003 version from NTIS.

Updates to the Philippines Inventory of Chemicals and Chemical Substances are now available. The updates are current through December 2002.

Updates to the Taiwan Toxic Chemical Substances List are now available. The updates are current through July 2002.

New additions to the file:

- High Production Volume (HPV) chemicals lists of Australia, ICCA, ECD and the United States (HELP HPV)
- Screening Information Data Set (SIDS) list (HELP SIDS)
- Substances that are classified as CERCLA Hazardous Substances in the Code of Federal Regulations (HELP CERHS)
- Known health hazards of specific chemicals (HELP HHAZ)
- Chemical and physical property data (HELP PRP)
- Information on storage, spill disposal, and environmental fate (HELP STOR)
- International information that may be required for the transportation, packaging, and labeling of chemicals (HELP TPL)
- German Water Hazard Class Substance List (HELP WGK)
- State of Louisiana Right-to-Know List of Extremely Hazardous Substances (HELP SLA)
- State of Minnesota Right-to-Know Hazardous Substances List (HELP SMN)
- Inventory Update Rule lists for 1986, 1990, 1994, and 1998 (HELP IUR)
- Violations to Miscellaneous Regulations or Advisory Lists (HELP VIO)

=> S L6

L7 1 L6

=> d his

(FILE 'HOME' ENTERED AT 11:11:52 ON 03 MAY 2003)

FILE 'REGISTRY' ENTERED AT 11:12:06 ON 03 MAY 2003

E 66893-81-0/CN

E POBN/CN

L1 1 S E3

E 66893-81-0/RN

L2 1 S E3

E 3376-24-7/RN

L3 1 S E3

E 3317-61-1/RN

L4 1 S E3

E 2564-83-2/RN

L5 1 S E3

FILE 'REGISTRY' ENTERED AT 11:15:40 ON 03 MAY 2003

SET TERMSET E#

DEL SEL Y

SEL L1 1 RN

L6 1 S E1/RN

SET TERMSET LOGIN

FILE 'CHEMLIST' ENTERED AT 11:15:45 ON 03 MAY 2003

L7 1 S L6

=> file ca

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

4.69

18.72

FILE 'CA' ENTERED AT 11:20:02 ON 03 MAY 2003

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 1 May 2003 VOL 138 ISS 19

FILE LAST UPDATED: 1 May 2003 (20030501/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l1

L8 144 L1

=> d l8 139-144 bib,ab

L8 ANSWER 139 OF 144 CA COPYRIGHT 2003 ACS

AN 92:102211 CA

TI Photolysis of alkylcobaloximes, methylsalen, cobalamines and coenzyme B12 in protic solvents: an ESR and spin-trapping technique study

AU Maillard, Ph.; Giannotti, C.
CS Inst. Chim. Subst. Nat., CNRS, Gif sur Yvette, 91190, Fr.
SO Journal of Organometallic Chemistry ~~(1979)~~, 182(2), 225-37
CODEN: JORCAI; ISSN: 0022-328X
DT Journal
LA English
AB The photolysis in protic solvents in the visible region >420 nm of several alkylcobaloximes, cobalamines, methylsalen, and coenzyme B12 was studied by ESR spectroscopy including the use of spin-trapping techniques involving 5,5'-dimethylpyrroline-N-oxide (DMPO), phenyl-N-tert-butyl nitron, and .alpha.-4-pyridyl-1-oxide-N-tert-butyl nitron. During the photolysis, H atoms are probably abstracted from the C(10) position of the corrin equatorial ligand in the case of coenzyme B12 and cobalamine derivs. The ESR spectra of the anaerobic photolysis of alkylcobaloximes in aprotic solvents in the presence of DMPO, followed by the addn. of air or pure O, provide evidence for intraligand radical spin-trapping reactions.

L8 ANSWER 140 OF 144 CA COPYRIGHT 2003 ACS

AN 92:31909 CA

TI Spin trapping and electron spin resonance detection of radical intermediates in the photodecomposition of water at titanium dioxide particulate systems

AU Jaeger, Calvin D.; Bard, Allen J.

CS Dep. Chem., Univ. Texas, Austin, TX, 78712, USA

SO Journal of Physical Chemistry (1979), 83(24), 3146-52

CODEN: JPCHAX; ISSN: 0022-3654

DT Journal

LA English

AB Spin trapping and ESR detection [with the traps .alpha.-Ph N-tert-Bu nitron and .alpha.-(4-pyridyl N-oxide) N-tert-Bu nitron] were used to detect free-radical intermediates formed during in situ irradiation of TiO₂ and platinized TiO₂ powders in aq. solns. Evidence for the production of OH radical (formed in the oxidation of H₂O) and HO₂ radical (probably formed in a redn. step) is presented. Other spin adducts, attributed to decomposition reactions of the spin traps, were also found. The results suggest an important role for photogenerated OH in many photocatalytic and photosynthetic processes using TiO₂ powders.

L8 ANSWER 141 OF 144 CA COPYRIGHT 2003 ACS

AN 92:2794 CA

TI Spin trapping of superoxide

AU Finkelstein, Eli; Rosen, Gerald M.; Rauckman, Elmer J.; Paxton, John

CS Med. Cent., Duke Univ., Durham, NC, 27710, USA

SO Molecular Pharmacology (1979), 16(2), 676-85

CODEN: MOPMA3; ISSN: 0026-895X

DT Journal

LA English

AB Due to conflicting reports in the literature, the spin trapping of superoxide by the nitron 5,5-dimethyl-1-pyrroline N-oxide (I) was reinvestigated. Superoxide could indeed be trapped and the 5,5-dimethyl-2-hydroxylpyrrolidinoxyl (II) and 5,5-dimethyl-2-hydroperoxypyrrolidinoxyl (III) adducts were distinguishable. In contrast to earlier work, III was highly unstable and decomposed into II. 2,5,5-Trimethyl-1-pyrroline N-oxide (TMPO), a spin trap structurally similar to I but lacking a .beta.-hydrogen, formed a stable nitroxide upon reaction with superoxide. Rate constants for the reaction of superoxide with I and TMPO were measured and indicated that spin trapping was an extremely inefficient method for the detection of superoxide. The new spin trap, .alpha.-4-pyridyl-1-oxide-N-tert-butyl nitron (POBN), was also capable of distinguishing the difference between superoxide and hydroxyl radical. The nitroxide formed upon the reaction of superoxide with POBN was unstable.

L8 ANSWER 142 OF 144 CA COPYRIGHT 2003 ACS
 AN 91:108398 CA
 TI The ESR spin trapping chemistry of .alpha.-(4-pyridyl 1-oxide)
 N-tert-butyl nitron and poly(phenyl-N-tert-butyl nitron)
 AU Wang, Yeeyang
 CS Univ. Georgia, Athens, GA, USA
 SO (1978) 194 pp. Avail.: Univ. Microfilms Int., Order No. 7914065
 From: Diss. Abstr. Int. B 1979, 39(12, Pt. 1), 5961
 DT Dissertation
 LA English
 AB Unavailable

L8 ANSWER 143 OF 144 CA COPYRIGHT 2003 ACS
 AN 90:5442 CA
 TI On spin trapping hydroxyl and hydroperoxy radicals
 AU Janzen, Edward G.; Nutter, Dale E., Jr.; Davis, Edward R.; Blackburn,
 Barry J.; Poyer, J. Lee; McCay, Paul B.
 CS Guelph-Waterloo Cent. Grad. Work Chem., Univ. Guelph, Guelph, ON, Can.
 SO Canadian Journal of Chemistry (1978), 56(17), 2237-42
 CODEN: CJCHAG; ISSN: 0008-4042
 DT Journal
 LA English
 AB The assignments of the HO.bul., HOO.bul., and ROO.bul. (R = alkyl) radical
 spin adducts of PhCH:N+(O-)CMe3 are discussed. Results of new expts.
 designed to test the assignments of the first two are described. The
 HO.bul. adduct assignment is correct. The relation between a.beta.Hand aN
 is detd. and gives a good fit for the 7 pairs of consts. reported for the
 HO.bul. adduct. The assignments for the HOO.bul. adduct may be correct
 but no proof is available.

L8 ANSWER 144 OF 144 CA COPYRIGHT 2003 ACS
 AN 89:23427 CA
 TI Spin trapping with .alpha.-pyridyl 1-oxide N-tert-butyl nitrones in
 aqueous solutions. A unique electron spin resonance spectrum for the
 hydroxyl radical adduct
 AU Janzen, Edward G.; Wang, Y. Y.; Shetty, Raghav V.
 CS Guelph Waterloo Cent. Grad. Work Chem., Univ. Guelph, Guelph, ON, Can.
 SO Journal of the American Chemical Society (1978), 100(9), 2923-5
 CODEN: JACSAT; ISSN: 0002-7863
 DT Journal
 LA English
 AB The spin-trapping chem. of .alpha.-4-pyridyl 1-oxide N-tert-Bu nitrones is
 described in aq. soln. as applied to the problem of detecting HO.bul.
 radical. Hyperfine-splitting consts. of the hydroxyl adduct are shown as
 a function of pH and H2O2 concn. A 2nd set of doublets was obsd. which
 were attributed to a 2nd nitroxide; this may be the hydroperoxy adduct,
 but this assignment is unsupported at this time.

=> s l2
 L9 144 L2

=> s l3
 L10 1014 L3

=> d l10 1009-1014 bib,ab

L10 ANSWER 1009 OF 1014 CA COPYRIGHT 2003 ACS
 AN 63:44176 CA
 OREF 63:7904d-e
 TI Derivatives of oxime. VIII. Polarographic reduction of O- and
 N-substituted oximes
 AU Zuman, P.; Exner, O.
 CS Ceskoslov. Akad. Ved, Prague

SO Collection Czech. Chem. Commun. (1965), 30(6), 1832-52
DT Journal
LA English
AB cf. CA 59, 15203h. In polarography with a dropping Hg electrode, aromatic N-substituted oximes (nitrones) (I) were reduced in acidic as well as in alk. media in a 4-electron wave to the secondary amines. The redn. proceeded through the corresponding Schiff base. The behavior of aromatic O-alkyl derivs. (II) in acidic solns. was similar to that of I whereas in alk. solns. II did not show any redn. wave. Aliphatic N-derivs. were reduced in acidic solns. only, and aliphatic O-derivs. were polarographically inactive. In all instances, both isomeric derivs. could be safely distinguished by polarography in alk. media. 28 references.

L10 ANSWER 1010 OF 1014 CA COPYRIGHT 2003 ACS

AN 54:110179 CA

OREF 54:20925d-i,20926a-i

TI Ozonation of carbon-nitrogen double bonds. I. Nucleophilic attack of ozone

AU Riebel, Alexander H.; Erickson, Ronald E.; Abshire, Claude J.; Bailey, Philip S.

CS Univ. of Texas, Austin

SO J. Am. Chem. Soc. (1960), 82, 1801-7

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA Unavailable

AB C-N double bonds of Schiff bases and nitrones were attacked by nucleophilic O₃. Thus, N-benzylidene-tert-butylamine (I) yielded the corresponding amide and oxazirane as noncleavage products, and BzH or BzOH and NH₄ type salts or N contg. materials as cleavage products. Cleavage was the major reaction with N-benzylideneaniline and N-cyclohexylideneisobutylamine. With N-phenylbenzaloxime and N-tert-butylbenzaloxime, O₃ gave initially BzH and the corresponding nitroso compds. The latter were oxidized by O₃ to nitro compds. O₃ was passed into 5 g. I in 130 ml. anhyd. AcOEt, the mixt. cooled to 0.degree. until 1.5 mole equivs. O₃ was absorbed, and the mixt. evapd. in vacuo at room temp. A slightly peroxidic powder (0.6 g.) pptd. on addn. of anhyd. Et₂O to the residue. An aq. soln. of the solid gave BzOH on addn. of HCl and tert-Bu-NH₂ on treatment with NaOH. The amine gave phenyltert-butylthiourea (m. 123-4.degree.) with PhNCO. Evapn. of the Et₂O soln. (after filtration of the powder) and crystn. of the residue from petr. ether gave 18% N-tert-butylbenzamide (II), m. 134-5.degree.. Distn. of the filtrate gave 0.5 g. BzH, 0.2 g. I, and 0.5 g. 2-tert-butyl-3-phenyloxazirane (III), b1 68-72.degree., identified by conversion to II. In a similar reaction, 2 mole equivs. O₃ was absorbed, the mixt. evapd. in vacuo to half vol., 100 ml. Et₂O added, the soln. extd. with 20% NaOH, washed, dried, and evapd. to give 24% II and 15% III. Acidification of the NaOH ext. gave 40% BzOH. When ozonized with O₃He the yields were 23% II, 12% III, and 21% BzOH. I with O₃ in CH₂Cl₂ gave 26% II, 5% tert-butylammonium benzoate (IV), sublimed at 120.degree., 9% III, and 28% tert-butylammonium chloride (V). Ozonation with O₃He gave 24% V, 20% II, and 8% III. I with O in CH₂Cl₂ gave no reaction. Following ozonolysis with 1, 1.5, and 2 mole equivs. O₃, 40, 9 and 0% I remained as shown by comparison of infrared bands at 908 and 962 cm.⁻¹ I (5 g.) in 130 CCl₄ with O₃ gave tert-butylamine, 14% II, 0.3 g. IV, 10% III, and a recovery of 10% I. With 2 mole equivs. O₃ followed by NaOH treatment as in the AcOEt expts., the yields were 21% II, 9% III, and 32% BzOH. Dibenzoyl peroxide (50 mg.), m. 107-8.degree., was isolated from the distn. residue on trituration with MeOH at -78.degree.. III (3.8 g.) in 75 ml. CH₂Cl₂ at 0.degree. with O₃ oxidized very slowly, 95% O₃ (1 mole equiv.) was recovered in a KI trap. The infrared spectrum of the mixt. showed essentially pure III with only very weak CO peak at 1700 cm.⁻¹ (BzH). III in CH₂Cl₂ with 20% NaOH brought about no change in III as shown by infrared spectra and nothing was obtained from the NaOH layer on acidification. Similar treatment of N-tert-butylbenzaloxime (VI) in CH₂Cl₂ with 20% NaOH gave quant. recovery of VI. Similar treatment of I

gave no change. Ozonation of 10 g. N-cyclohexylidene isobutylamine (VII), prepd. in 79% yield by refluxing 1 mole cyclohexanone, 2 moles iso-BuNH₂, and 250 ml. C₆H₆ 3 days with removal of H₂O gave 48% cyclohexanone and 0.5 g. peroxidic material, believed to be 2-isobutyl-3,3-pentamethyleneoxazirane, b.p. 55-60.degree.. When an aliquot of the mixt. was poured into NaI soln. the iodine released was treated with thiosulfate, which indicated 23% active O material, assumed to be largely oxazirane. Treatment of the remainder of the mixt. as previously described gave 0.2 g. amine salt, assumed to be isobutylammonium chloride. N-Benzylideneaniline (VIII) (5 g.) with O₃ in 60 ml. glacial AcOH at 17.degree. absorbed 2 moles O₃ and gave 0.33 g. mixt. of PhNO₂ and BzH, 39% benzoic acid, and 1.7 g. powdery solid, insol. in Et₂O, but sol. in AcOH, mineral acids, MeOH, and C₅H₅N. The solid with Zn dust gave aniline. VIII treated with NaI and titrated with Na₂S₂O₃ indicated 16% active O. VIII (5 g.) in 100 ml. anhyd. AcOEt at 0.degree. on absorption of 2 moles O₃ gave 45% BzOH and 0.35 g. mixt. of PhNO₂ and BzH. VIII (5 g.) in anhyd. CH₂Cl₂ with 1 and 2 mole equivs. O₃ at 0.degree. showed considerable amts. of BzH and small amts. of PhNO₂. Cryst. material (5 g.) similar to that obtained by ozonation in other solvents was obtained on absorption of 2 equivs. O₃ followed by cooling to -78.degree.. With MeOH solvent, benzaldehyde was isolated as the phenylhydrazone (54%). When the mixt. was not reduced with NaI but allowed to reach room temp., the yield of benzaldehyde phenylhydrazone was 24%. Similar results were obtained with an O₃-N mixt. N-Benzylidene-m-nitroaniline treated with O₃ and the cold mixt. reduced with NaI gave benzaldehyde as the phenylhydrazone (40%). N-Phenylbenzaldoxime (IX) (5 g.) in 75 ml. CH₂Cl₂ with 2 mole equivs. O₃ at -78.degree. developed a green color characteristic of PhNO which disappeared toward the end of the reaction. After evapn. of the solvent in vacuo, the residue was treated with 4 g. semicarbazide-HCl, 40 g. AcONa, 50 ml. H₂O, and 50 ml. Skellysolve B, the mixt. shaken, kept cold several hrs., and then filtered to yield 90% benzaldehyde semicarbazone. The org. layer on drying and distg. gave 66% PhNO₂. In some runs low yields of BzOH were obtained from partial autoxidn. of BzH. With O₃-N, 6.2 g. IX in 70 ml. CH₂Cl₂ gave 51% BzH and 84% PhNO₂, as indicated by infrared analysis. With one mole equiv. O₃ (O₃-O mixt.), 43% BzH and 30% PhNO were obtained. The reaction repeated with O₃ (O₃-He mixt.) gave a PhNO fraction which was not isolated, 52% benzaldehyde semicarbazone, and 27% IX. The infrared spectra of BzH, PhNO, PhNO₂, BzOH, and IX were detd. at a no. of known concns. and Beer's law plots of various bands obtained. While 6 g. IX was treated with 2 mole equivs. O₃ in CH₂Cl₂ at 0.degree., 10 1-ml. aliquots were withdrawn and their infrared spectra obtained, the concn. of BzH, PhNO, PhNO₂, and BzOH being detd. from Beer's plots and found to be 65, 35, 27, and 0%, resp., for 1 mole equiv. and 68, 0, 82, and 15% after 2 mole equivs. O₃ was absorbed. Absorption of 2 moles O₃ (O₃-He mixt.) gave 94% BzH and 98% PhNO₂. The yields obtained on gas chromatography of the products through bis(2-ethylhexyl) sebacate and diisodecyl phthalate columns at 163.degree. were 49% BzH, 20% PhNO, and 45% PhNO₂ for 1 mole equiv. O₃ and 100, 0, and 100% for 2 mole equivs. O₃ absorption. PhNO (5.1 g.) in 50 ml. of CH₂Cl₂ at 0.degree. was completely ozonized with O₃-O; 1 mole equiv. O₃ was absorbed, the infrared spectra showing only PhNO₂. Distn. in vacuo gave 87% PhNO₂. VI (5 g.) in 40 ml. CH₂Cl₂ at -78.degree. with O₃ (O₃-O mixt.) gave Me₃CNO₂ (X), b. 120-5.degree., 54% BzH, and 21% BzOH. In a 2nd run the BzH was isolated as the phenylhydrazone (85%). The reaction followed by infrared analysis showed that BzH and X were present in approx. equal quantities until near the end of the reaction, when some autoxidn. of BzH occurred. The corrected yields were 42% BzH, 38% X, and 46% VI after 1 mole equiv. O₃ was absorbed, 90% BzH after 1.8 mole equivs. O₃, and 46% BzH, 41% BzOH, and 89% X after 2 mole equivs. The course of the reaction was followed by obtaining gas chromatographs of aliquots at 50.degree., 128.degree., and 163.degree. on the same columns as previously. Corrected yields gave 54% BzH, 1% PhNO, and 52% .times. after 1 mole equiv. O₃ and 70, 0, and 88% after 2 mole equivs. O₃ was absorbed.

L10 ANSWER 1011 OF 1014 CA COPYRIGHT 2003 ACS

AN 52:97888 CA

OREF 52:17226g-i,17227a

TI Preparation of oxaziranes by irradiation of nitrones

AU Splitter, J. S.; Calvin, M.

CS Univ. of California, Berkeley

SO J. Org. Chem. (1958), 23, 651

CODEN: JOCEAH; ~~ISSN:~~ 0022-3263

DT Journal

LA Unavailable

AB .alpha.-(p-Nitrophenyl)-N-ethylnitrone (I), .alpha.-(p-nitrophenyl)-N-tert-butyl-nitrone (II), and .alpha.-phenyl-N-tert-butyl-nitrone (III) apparently formed the corresponding oxazirane (IV) (V) (VI), when irradiated. The results were as follows (nitrone, mg. of nitrone, solvent, ml. of solvent, irradiation time, formed, % oxazirane, mode of detn. of yield given): I, 10, MeCN, 70, 1 hr., IV, 35, isolated; II, 10, alc., 70, 25 min., V, 40, isolated; III, 10, MeCN, 50, 2 hrs., VI, 95, from active O content and reversion to III. The oxazirane structure for IV, V, and VI was established by comparison in each case with the oxazirane obtained by oxidation of the corresponding imine. The properties used for identification of each are as follows: IV, ultraviolet and infrared spectra; V, m. 58-60.degree., and mixed m.p., ultraviolet spectrum, 95% active O; VI, ultraviolet spectrum, almost quant. isomerization to the nitrone III, 90% active O. Although .alpha.-(p-dimethylaminophenyl)-N-phenyloxazirane could not be synthesized by the oxidation of the imine, the properties and reactions of the products of the irradiation of several N, .alpha.-diarylnitrones are consistent with the oxazirane structure. Thus it seems evident that the initial product in the irradiation of nitrones is an oxazirane. The oxazirane is in general at a higher energy level than the nitrone. This photochem. reaction constitutes a conversion and storage of electromagnetic energy as chem. energy.

L10 ANSWER 1012 OF 1014 CA COPYRIGHT 2003 ACS

AN 52:40503 CA

OREF 52:7263d-i,7264a-i,7265a-h

TI Preparation and properties of oxaziranes

AU Emmons, Wm. D.

CS Rohm & Haas, Huntsville, AL

SO J. Am. Chem. Soc. (1957), 79, 5739-54

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA Unavailable

AB cf. C.A. 51, 7343h. [Throughout this abstr. R = Me₃C and R' = tert-C₈H₁₇.] The following imines were prepd. by condensation of the appropriate amine with a ketone or aldehyde (b.p./mm. or m.p., and n₂₀D given): CH₂:N R, 65.degree./740, 1.4151; CH₂:NR', 50-2.degree./13, 1.4381; PhCH:NR, 90-2.degree./11, 1.5211; p-O₂NC₆H₄CH:N R, 73-5.degree. (petr. ether), -; p-O₂N C₆H₄CH:NR', -(noncrystallizable oil), 1.5430; p-O₂NC₆H₄CH:NCHMe₂ (I), 54-5.degree., -; p-O₂NC₆H₄CH:NEt, 75-6.degree., -; iso-PrCH:NR, 51-3.degree./83, 1.4078; iso-PrCH:NBu, 67.degree./68, 1.4151; iso-PrCH:NCHMePh, 68.degree./0.8, 1.4975; iso-BuMeC:NPr, 65.degree./22, 1.4272; (RN:CH₂)₂ (II), 52-3.degree., -; BuEtCHCH:NBu, 87.degree./8, 1.4338; 2-C₅H₄NCH:NR, 56-8.degree./0.2, 1.5335; PhCH:NR' (III), 100.degree./0.4, 1.5162; iso-PrMeC:NPr, 48.degree./26, 1.4230; EtMeC:NCH₂CH:CH₂, 94.degree./100, -; Et₂C:NEt, 52-4.degree./54, 1.4230; Me₂C:NC₆H₁₃, 53-5.degree./5.0, 1.4319; iso-PrCH:NCH₂CHMe₂, 57.degree./64, 1.4097; Et₂C:NCHMePh, 64.degree./0.2, 1.5050. CH₂Cl₂ (100 cc.) treated with stirring with 30.0 cc. 90% H₂O₂ and 2 drops H₂SO₄ and then dropwise with cooling during 0.5 hr. with 135 g. Ac₂O, stirred 15 min. at 0.degree. and 30 min. at room temp., added dropwise during 0.5 hr. with stirring to 85 g. CH₂:NR in 100 cc. CH₂Cl₂, kept at room temp. overnight, washed, dried, and fractionated gave 46.4 g. 2-tert-butyloxazirane (IV), b₇₅ 52-4.degree., n₂₀D 1.4150, contg. 93.8% active O (detd. with KI and AcOH).

PhCH:NR (V) (80.5 g.) in 100 cc. CH₂Cl₂ treated dropwise with stirring with 15 cc. 90% H₂O₂, 50 cc. CH₂Cl₂, and 1 drop H₂SO₄ in 67.2 g. Ac₂O and worked up after standing overnight yielded 63.1 g. 3-Ph deriv. (VI) of IV, b.p. 61-3.degree., n_D 1.5081, contg. 95.6% active O. CH₂Cl₂ (100 cc.), 25.3 cc. 90% H₂O₂, 2 drops H₂SO₄, and 114 g. Ac₂O added dropwise to 71 g. II in 75 cc. CH₂Cl₂, kept overnight, and worked up gave 40 g. (crude) bis(2-tert-butyloxazirane), m. 53-6.degree. (petr. ether at -78.degree.), which chromatographed on silica gel gave material, m. 82-4.degree. (presumably meso), and a 2nd fraction, m. 42-3.degree. (presumably dl). Similarly were prepd. the following substituted oxaziranes (substituents in 3, 3, and 2-positions, % yield, b.p. or m.p., mm., active O, and n_D given): H, H, R' (VII), 69, 70-2.degree./6, 99.2, 1.4445; Ph, H, R', 67, -, -, 1.5019; p-O₂NC₆H₄, H, iso-Pr, 60, 46-8.degree., 92.0, -; p-O₂NC₆H₄, H, Et, 97, 34-5.degree., 99.3, -; p-O₂NC₆H₄, H, R, 78, 65-6.degree., 99.4, -; iso-Pr, H, R (VIII), 71, 68-70.degree./39, 99.8, 1.4152; iso-Pr, H, Bu (IX), 65, 65-7.degree./10, 91.5, 1.4178; BuEtCH, H, Bu, 83, -, 98.7, 1.4350; iso-Pr, H, CHMePh (X), 80, -, 99.7, 1.4956; iso-Bu, Me, Pr (XI), 73, 61.degree./8, 93.6, 1.4267; p-O₂NC₆H₄, H, R', 66, 54-6.degree., 96.9, -; Me, iso-Pr, Pr, 64, 60.degree./15, 94.7, 1.4222; Bu, H, H, 74, 43.degree./20, 98.1, 1.4178; iso-Pr, H, R', 78, -, 99.6, 1.4385; Me, Et, CH₂CH:CH₂, 59, 51.degree./6, 91.2, 1.4413; Et, Et, Et (XII), 56, 62.degree./19, 97.7, 1.4225; Me, Me, C₆H₁₃, 14, 58.degree./3, 94.7, 1.4278; iso-Pr, H, iso-Bu (XIII), 50, 53.degree./12, 92.0, 1.4150; Et, Et, MePhCH (XIV), 91, -, 90.1, 1.5038; 2-pyridyl, H, R, 75, 68-70.degree./0.4, 96.1, 1.5010. CH₂Cl₂ (50 cc.), 9.8 cc. 90% H₂O₂, 1 drop H₂SO₄, and 44.1 g. Ac₂O added with stirring to 45.9 g. N-cyclohexylideneisobutylamine in 50 cc. CH₂Cl₂ gave 41.1 g. 2-isobutyl-3,3-pentamethyleneoxazirane (XV), b.p. 59-62.degree., n_D 1.4569, contg. 97.2% active O; after 1 month at room temp. the active O had dropped to 32% and a lower aq. layer had sep'd.; the org. layer (21 g.) distd. gave 5.1 g. XV, 7.5 g. cyclohexanone, and 3.5 g. yellow liquid, b.p. 68-70.degree., apparently a condensation product of cyclohexanone with 2 moles Me₂CHCH:NH. VI (177 g.) added dropwise with stirring and cooling to 100 cc. H₂O, 1 l. MeOH, and 60 cc. H₂SO₄, warmed, stirred 20 hrs. at room temp., poured into 1 l. H₂O, extd. with Et₂O, and the ext. distd. gave 98.8 g. BzH, b.p. 75.degree., and left 1.2 g. PhCH:N(O)R (XVI), m. 75.degree.; the original aq. acidic layer treated with 150 g. NaOH in 300 cc. H₂O and extd. 3 days with Et₂O yielded 73 g. RNHOH (XVII), m. 64-5.degree. (petr. ether), oxidized in air to blue RNO. III (233 g.) stirred 3 days at room temp. with H₂SO₄ in aq. MeOH gave similarly 86 g. BzH and 120 g. (crude) R'NHOH (XVIII), b.p. 50-3.degree., m. 40-2.degree. (sublimed), oxidized by air to R'NO. XVII (4.5 g.) and 5.3 g. BzH heated at 45.degree., kept 1 hr. at 50-60.degree., and the product isolated with 50 cc. CH₂Cl₂ gave 5.5 g. XVI, m. 75-6.degree. (petr. ether). VI (8.8 g.) in 100 cc. dry MeCN refluxed 3 days and the resulting nitron hydrolyzed in the usual manner gave essentially 100% BzH and XVII. XVIII (14.5 g.) and 10.6 g. BzH heated 0.5 hr. on the steam bath and the product isolated with 50 cc. CH₂Cl₂ gave 15.8 g. PhCH:N(O)R' (XIX), m. 103-4.degree., hydrolyzed with H₂SO₄ in aq. MeOH to 100% BzH and XVIII. XVII (8.9 g.) and 4.2 g. 30% aq. (CHO)₂ shaken 15 min. at room temp. and the product isolated with 100 cc. CH₂Cl₂ gave 4.7 g. (crude) [RCN(O):CH]₂, creamcolored, m. 193-5.degree. (ligroine). p-O₂NC₆H₄CHO (9.1 g.), 8.9 g. XVII, and 100 cc. C₆H₆ refluxed 10 hrs. under an H₂O-separator gave 10.0 g. p-O₂NC₆H₄CH:N(O)R, yellow, m. 134-5.degree. (3:1 Et₂O-petr. ether). XVIII (14.5 g.), 15.1 g. p-O₂NC₆H₄CHO, and 125 cc. C₆H₆ refluxed 20 hrs. under an H₂O-separator yielded 12.8 g. p-O₂NC₆H₄CH:N(O)R', m. 119-21.degree. (petr. ether). I refluxed 14 hrs. in 25 cc. PhMe, evapd., and chromatographed on silica gel gave a mixt. of p-O₂NC₆H₄CHO, an unknown material, and 2.7 g. p-O₂NC₆H₄CH:N(O)CHMe₂, m. 98-100.degree. (petr. ether). VI (17.7 g.) in 50 cc. Et₂O reduced with 3.8 g. LiAlH₄ in 200 cc. Et₂O gave 14.6 g. V, b.p. 48.degree.. VI (8.9 g.) added dropwise with stirring to 25 g. KI, 100 cc. H₂O, 200 cc. EtOH, and 40 cc. AcOH, treated less than 15 min. with NaHSO₃, basified, and extd. with Et₂O gave 6.5 g. V. XVI (5.6 g.) in 50 cc. Et₂O reduced with 1.2 g. LiAlH₄ in 200 cc. Et₂O yielded 4.3 g.

PhCH₂NROH, m. 71-3.degree. (ligroine). XIX (7.5 g.) in 50 cc. Et₂O reduced with 1.2 g. LiAlH₄ in 200 cc. Et₂O and decompd. with HCl gave 4.5 g. PhCH₂NR'OH (XX). HCl, m. 172-4.degree. (EtOAc). XX.HCl and NaOH in aq. MeOH gave XX, noncrystallizable oil. VII (15.7 g.) in 50 cc. Et₂O reduced with 3.8 g. LiAlH₄ in 150 cc. Et₂O gave 10.4 g. R'NHMe, b₁₉ 56-8.degree., n_{20D} 1.4305; HCl salt, m. 158-9.degree. (EtOAc). R'N:CH₂ reduced with LiAlH₄ gave 74% R'NHMe. XI (27.6 g.) and 30.4 g. brucine in 80 cc. CH₂Cl₂ refluxed 16 hrs. and filtered gave 28.5 g. brucine N-oxide, m. 194.degree. (decompn.); the filtrate washed, dried, and distd. gave 8.1 g. (crude) XI which fractionated yielded 4.3 g. XI, b_{8.0} 60.degree., n_{20D} 1.4260, .alpha._{24D} -2.80.degree. (neat). VI (35.4 g.) in 100 cc. dry C₆H₆ treated dropwise with stirring and cooling with 28.4 g. Et₂O.BF₃ in 50 cc. C₆H₆, kept 1.5 hrs. at room temp., and filtered yielded 40 g. BF₃ salt of the unstable isomer (presumably cis) of XVI, m. 80-8.degree. (CH₂Cl₂ at -80.degree.), converted on recrystn. from hot EtOAc to the stable isomer (presumably trans) of XVI, m. 135-7.degree.. XVI and Et₂O.BF₃ in Et₂O at room temp. gave an essentially quant. yield of trans-XVI. At room temp. cis-XVI underwent isomerization to trans-XVI. 2-Butyloxazirane (1.0 g.) and 5.0 g. 2,4-(O₂N)₂C₆H₃NHNH₂ in 25 cc. concd. H₂SO₄, 36 cc. H₂O, and 125 cc. EtOH kept overnight gave 4.2 g. mixed 2,4-dinitrophenylhydrazones of CH₂O and PrCHO; the aq. filtrate basified and distd., the aq. alc. distillate shaken 1 hr. at room temp. with 1.35 g. PhNCS, and the product isolated with CH₂Cl₂ yielded 1.2 g. PhNHCSNH₂, m. 152-4.degree.. IX (1.4 g.) gave similarly 4.6 g. mixed 2,4-dinitrophenylhydrazones of equal amts. of PrCHO and iso-PrCHO, and 64% PhNHCSNH₂. IV (1.0 g.) under the same conditions yielded 4.0 g. 2,4-dinitrophenylhydrazones of equimolar amts. of CH₂O and Me₂CO, and 60% MeNH₂ (isolated as 1.0 g. PhNHCSNHMe, m. 111-12.degree.). X (1.9 g.) gave similarly 4.6 g. mixed 2,4-dinitrophenylhydrazones of equal amts. of AcH and iso-PrCHO; the alk. filtrate steam-distd. gave 0.8 g. PhNH₂ (tribromide, m. 120.degree.). X (19.1 g.) added dropwise with cooling and stirring to 8.6 g. KOH in 100 cc. (CH₂OH)₂, kept 1 hr. at 0.degree., allowed to warm spontaneously to 45.degree., and heated 1 hr. at 60.degree./5.0 mm. gave 4.1 g. iso-PrCHO (2,4-dinitrophenylhydrazone, m. 179-81.degree.); the mixt. poured into 300 cc. H₂O, extd. with CH₂Cl₂, and the ext. worked up yielded 1.5 g. BzCH:CHCHMe₂, m. 139-40.degree.; the mother liquor yielded 3.1 g. PhAc, b_{12.0} 83-5.degree.. VI (5.3 g.) added at room temp. with stirring under N to 12.0 g. Fe(NH₄)(SO₄)₂.6H₂O (XXI) in 100 cc. H₂O and the product isolated after 2 hrs. with CH₂Cl₂ gave 5.2 g. BzNHR, m. 134.degree.. A similar run with only 1.2 g. XXI gave 5.3 g. (crude) BzNHR; the petr. ether washings from the crude product gave 1.5 g. unchanged VI. VII (4.7 g.) and 1.2 g. XXI gave similarly 4.1 g. HCONHR', b_{0.5} 84.degree., n_{20D} 1.4555. XII (12.9 g.) added with stirring to 8.0 g. XXI in 100 cc. H₂O under He while passing the effluent gases through Drierite, Dry Ice-Me₂CO, and liquid N traps, the mixt. stirred 36 hrs. at room temp., extd. 3 days with CH₂Cl₂, and the ext. distd. gave 4.3 g. Et₂CO, b. 96-8.degree., and 3.2 g. EtCONHET, b_{0.5} 65.degree., n_{20D} 1.4369; the cold traps contained C₄H₁₀ and 3:1 C₂H₆-C₂H₄; the aq. soln. from a duplicate run washed with Et₂O, basified, and distd. gave 0.055 mole NH₃. XIV (15.7 g.) and 16 g. XXI in 150 cc. H₂O stirred 40 hrs. under N at room temp. gave C₄H₁₀ and 2:1 C₂H₆-C₂H₄, a trace of PhAc, b_{12.0} 85.degree., and 11.2 g. EtCONHCHMePh, b_{0.05} 121.degree., n_{20D} 1.5262, m. 58-60.degree.; the yield of NH₃ was 2%. XIII (14.3 g.) and 8.0 g. XXI in 100 cc. H₂O stirred 8 hrs. under He gave 1:1 C₃H₈-C₃H₆ and 8.5 g. iso-BuNH₂CH, b_{0.1} 60.degree., n_{20D} 1.4388. VIII (14.3 g.), 16 g. XXI, and 150 cc. H₂O stirred 16 hrs. under He gave 3:1 C₃H₈-C₃H₆ and 8.4 g. HCONHR, b_{0.2} 48.degree., n_{20D} 1.4326. VI (34.4 g.) added dropwise during 2 hrs. at 200.degree. to a vertical glass tube packed with glass helices and entrained with 50 cc. N/min. and the effluent gases passed through an ice and Dry Ice-Me₂CO trap gave 7.2 g. Me₂C:CH₂ contaminated with traces of NO, CO₂, and RNO; the ice trap contained 27 g. viscous liquid which yielded 8.8 g. PhCH:NOH and 4.1 g. XVI. VII (30.0 g.) pyrolyzed during 2 hrs. at 200.degree. gave 19.7 g. HCONHR', b_{0.5} 82.degree., n_{20D} 1.4552. VII (15 g.) in 50 cc. HCONMe₂ refluxed overnight, poured into H₂O, and extd. with CH₂Cl₂ gave 11.2 g.

HCONHR'. XV (20.0 g.) pyrolyzed during 1 hr. at 300.degree. yielded a trace of cyclohexanone and 16.5 g. N-isobutylcaprolactam, b0.7 75.degree., n20D 1.4750. VIII (25.3 g.) pyrolyzed during 2 hrs. at 250.degree. gave 15.9 g. iso-PrCONHR, m. 118-20.degree. (also obtained from iso-PrCOCl and RNH2), and 3.2 g. unchanged VIII. XIII (20.0 g.) pyrolyzed at 300.degree. gave 9.7 g. iso-Bu-(iso-Pr)NOCH (XXII), b3.0 78-80.degree., n20D 1.4409, and 4.9 g. iso-PrCONHCH2CHMe2 (XXIII), m. 43-5.degree., b0.2 85-8.degree.. iso-BuNHCHMe2 (8.0 g.) treated with stirring with 10.5 g. CCl3CHO and kept at room temp. overnight yielded 7.5 g. XXIII, b1.0 65.degree., n20D 1.4411. Iso-PrCOCl (11.2 g.) in 100 cc. dry Et2O treated with stirring with 14.6 g. iso-BuNH2, refluxed 1 hr., and worked up gave 13.0 g. XXIII, m. 43-5.degree., b0.1 82.degree.. XI (100 g.) pyrolyzed during 4 hrs. at 300.degree. yielded 67.0 g. mixt. of 64% iso-BuCONMePr (b5.0 93.degree., n20D 1.4437, from iso-BuCOCl and MeNHPr) and 36% iso-BuPrNAC (b5.0 91.degree., n20D 1.4440, from iso-BuNHPr and Ac2O). XI (25.0 g.) pyrolyzed at 300.degree. yielded 13.9 g. mixt. of 39% iso-PrPrNAC (b5.0 68-70.degree., n20D 1.4437, from iso-PrNHPr and Ac2O) and 61% iso-PrCONMePr (b5.5 67.degree., n20D 1.4409, from iso-PrCOCl and MeNHPr). XI (27.6 g.) refluxed 2 hrs. under N at 168 to 128.degree. and the effluent gases passed over aq. H3BO3 showed the formation of 0.057 mole NH3; the liquid product distd. gave 16.1 g. iso-BuAc, b. 114-16.degree., 0.8 g. unreacted XI, and 1.0 g. mixed amides, b3.0 68-70.degree.. XIII (25.0 g.) refluxed 3 hrs. under N at 165 to 105.degree. yielded 8.0 g. iso-PrCH:NCH2CHMe2, b47 60.degree..

L10 ANSWER 1013 OF 1014 CA COPYRIGHT 2003 ACS

AN 52:35153 CA

OREF 52:6304h-i,6305a-b

TI Kinetics of the thermal isomerization of 2-tert-butyl-3-phenyloxazirane

AU Hawthorne, M. Frederick; Strahm, R. Donald

CS Rohm & Haas Co., Huntsville, AL

SO J. Org. Chem. (1957), 22, 1263-4

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA Unavailable

AB This kinetic study was designed to det. the enthalpy and entropy of activation for the rearrangement of 2-tert-butyl-3-phenyloxazirane (I), in diethylene glycol diethyl ether (II) over a 40.degree. temp. range. I was further purified by chromatography on silica gel using CH2Cl2 followed by vacuum distn. The ultraviolet spectrum of I in MeCN showed only end absorption. When repurified, II b33 94-6.degree., n20D 1.4115. Similarly pure N-tert-butylbenzaldoxime (III) was obtained, m. 75-7.degree., .lambda. 289 m.mu., .epsilon. 16,8000. Solns. of I (0.1 to 0.44M) in pure II were prepd. in 10-ml. flasks, the flasks placed at zero time in the appropriate thermostat, at intervals aliquots were removed and delivered to a vol. of MeCN which was made up to 10 ml., optical density readings were made at 298 m.mu. and the concn. of III computed. Points were taken until the reaction had progressed to 75% completion. After several days (or weeks at lower temp.) the rearrangement of I to III was found to be complete. First order plots were prepd. by plotting log [I] against time. The following first order consts. were obtained (temp., initial I concn. in mole/l., k1 (sec.-1) .times. 107 are given): 100.0.degree., 0.437, 545; 100.degree., 0.252, 537; 85.0.degree., 0.116, 530; 85.0.degree., 0.241, 119; 85.0.degree., 0.229, 113; 85.0.degree., 0.120, 113; 85.0.degree., 0.115, 117; 85.0.degree., 0.233, 5.40; 60.0.degree., 0.127, 5.40. The .DELTA. H was found to be 28 kcal./mole between 60 and 100.degree.. The entropy of activation was -3 .+- .1 entropy units, a value which indicated that the structures of oxazirane reactant and nitron product were equally rigid. The slight neg. value may indicate increased solvation of the transition state due to the development of a strong N .fwdarw. O dipole.

L10 ANSWER 1014 OF 1014 CA COPYRIGHT 2003 ACS

AN 51:39192 CA

OREF 51:7343h-i,7344a

TI Synthesis of oxaziranes
 AU Emmons, Wm. D.
 CS Redstone Arsenal, Huntsville, AL
 SO J. Am. Chem. Soc. (1956), 78, 6208-9
 CODEN: JACSAT; ISSN: 0002-7863
 DT Journal
 LA Unavailable
 AB Certain azomethines which are sluggish toward acid hydrolysis can be oxidized in good yield with (AcO)₂ to oxaziranes (I), RR1.C.NR2.O, which resemble org. peroxides. Some typical examples of I are (R, R1, R2, b.p./mm., % yield, and nD₂₀ given): H, H, tert-Bu, 52.degree./75, 46, 1.4150; Ph, H, tert-Bu, 63.degree./0.5, 71, 1.5081; H, H, tert-C₈H₁₇, 64.degree./6, 69, 1.445; p-O₂NC₆H₄, H, Et, - (m. 34-5.degree.), 95, -; Me, iso-Bu, Pr, 64.degree./7, 63, 1.4277. 2-tert-Butyl-3-phenyloxazirane (II) with H₂SO₄ in aq. MeOH yielded 100% BzH and Me₃CNHOH (III), m. 64.degree.. III and BzH yielded the nitron, PhCH:N(O)CMe₃ (IV), m. 76.degree.. II with LiAlH₄ in Et₂O yielded only Me₃CN:CHPh; IV yielded PhCH₂N(OH)CMe₃, m. 72.degree.. 2-Propyl-3-methyl-3-isobutyloxazirane was partially resolved with brucine in boiling CH₂Cl₂.

=> s l11

L11 NOT FOUND

The L-number entered has not been defined in this session, or it has been deleted. To see the L-numbers currently defined in this session, enter DISPLAY HISTORY at an arrow prompt (=>).

=> d his

(FILE 'HOME' ENTERED AT 11:11:52 ON 03 MAY 2003)

FILE 'REGISTRY' ENTERED AT 11:12:06 ON 03 MAY 2003

E 66893-81-0/CN

E POBN/CN

L1 1 S E3

E 66893-81-0/RN

L2 1 S E3

E 3376-24-7/RN

L3 1 S E3

E 3317-61-1/RN

L4 1 S E3

E 2564-83-2/RN

L5 1 S E3

FILE 'REGISTRY' ENTERED AT 11:15:40 ON 03 MAY 2003

SET TERMSET E#

DEL SEL Y

SEL L1 1 RN

L6 1 S E1/RN

SET TERMSET LOGIN

FILE 'CHEMLIST' ENTERED AT 11:15:45 ON 03 MAY 2003

L7 1 S L6

FILE 'CA' ENTERED AT 11:20:02 ON 03 MAY 2003

L8 144 S L1

L9 144 S L2

L10 1014 S L3

=> s l2

L11 144 L2

=> s l1

L12 144 L1

E 66893-81-0/CN
E POBN/CN
L1 1 S E3
E 66893-81-0/RN
L2 1 S E3
E 3376-24-7/RN
L3 1 S E3
E 3317-61-1/RN
L4 1 S E3
E 2564-83-2/RN
L5 1 S E3

FILE 'REGISTRY' ENTERED AT 11:15:40 ON 03 MAY 2003

SET TERMSET E#
DEL SEL Y
SEL L1 1 RN
L6 1 S E1/RN
SET TERMSET LOGIN

FILE 'CHEMLIST' ENTERED AT 11:15:45 ON 03 MAY 2003

L7 1 S L6

FILE 'CA' ENTERED AT 11:20:02 ON 03 MAY 2003

L8 144 S L1
L9 144 S L2
L10 1014 S L3
L11 144 S L2
L12 144 S L1
L13 1014 S L3

=> s l4

L14 825 L4

=> d l14 820-825 bib,ab

L14 ANSWER 820 OF 825 CA COPYRIGHT 2003 ACS

AN 64:75320 CA

OREF 64:14065e

TI Mass spectra of N-oxides

AU Grigg, R.; Odell, B. G.

CS Univ. Chem. Lab., Cambridge, UK

SO J. Chem. Soc., B, Phys. Org. (1966), (3), 218-19

DT Journal

LA English

AB Large (M-16) ions are not characteristic of the N-oxide groups in 1-pyrroline N-oxides but are of some diagnostic value in aromatic N-oxides.

L14 ANSWER 821 OF 825 CA COPYRIGHT 2003 ACS

AN 64:51877 CA

OREF 64:9667e-f

TI The periodate oxidation of nitrones

AU Qureshi, A. K.; Sklarz, B.

CS Imp. Coll. Sci. Technol., London

SO J. Chem. Soc., Org. (1966), (4), 412-15

DT Journal

LA English

AB The periodate oxidn. of some 1-pyrroline 1-oxides with two substituents at C-5 but unsubstituted at C-2 leads to a series of 4-nitrosopentanoic acids. Evidence is adduced for the course of the reaction. An N-alkylhydroxy amino compd. is oxidized in chloroform to the nitroso compd. by tetraethylammonium periodate, a potentially useful reagent, sol. in various org. solvents.

L14 ANSWER 822 OF 825 CA COPYRIGHT 2003 ACS

AN 62:90756 CA

OREF 62:16185g-h,16186a

TI Oxidative phosphorylation, by phosphate adducts of compounds with a C=N+ double bond

AU Clark, V. M.; Hutchinson, D. W.; Wilson, D. E.

CS Univ. Chem. Lab., Cambridge, UK

SO Angew. Chem. (1965), 77(6), 259-60

DT Journal

LA German

AB I-III, on treatment with (Bu₄N)3PO₄ or (Me₃SO)3PO₄ in non-aq. solvents, gave adducts which could be detd. spectroscopically. With 100% excess phosphate, followed by oxidn. with Br or KMnO₄, 25% pyrophosphate was formed. The adduct of Ib with an equiv. amt. of phosphate, on reaction with (Bu₄N)2PhPO₄ and KMnO₄, gave 25% monophenyl pyrophosphate. Addn. of Br to a soln. of the adduct of III in EtOH yielded 10% EtH₂PO₄. A reaction scheme was proposed.

L14 ANSWER 823 OF 825 CA COPYRIGHT 2003 ACS

AN 57:62584 CA

OREF 57:12408d-e

TI Studies in the pyrroline series. I. The proton mag-netic resonance spectra of some pyrrolines

AU Bonnett, R.; McGreer, D. E.

CS Univ. Brit. Columbia, Vancouver

SO Can. J. Chem. (1962), 40, 2177-80

DT Journal

LA Unavailable

AB The proton magnetic spectra of 2,4,4-trimethylpyrroline, 5,5-dimethylpyrroline, 2-methylpyrroline, 2,2,3,3-tetramethylpyrroline, 2-phenyl3,3-dimethylpyrroline, 3,3-dimethylpyrroline N-oxide, and 5,5-dimethylpyrroline N-oxide was measured. The proton magnetic resonance spectra strongly reinforce previous conclusions that the double bond is in the .DELTA.1 position.

L14 ANSWER 824 OF 825 CA COPYRIGHT 2003 ACS

AN 55:33039 CA

OREF 55:6466d-f

TI Cycloaddition of .alpha.,.beta.-unsaturated esters to nitrones

AU Delpierre, G. R.; Lamchen, M.

CS Univ. Cape Town, S. Afr.

SO Proc. Chem. Soc. (1960) 386-7

DT Journal

LA Unavailable

AB EtO₂CCH:CH₂ added to 5,5-dimethyl-1-pyrroline 1-oxide (I) to give Me₂C.CH₂.CH₂.N.CH.CH₂.CH(CO₂Et).O. The structure of this product was confirmed by redn. with LiAlH₄ in boiling tetrahydrofuran to give 2,2-dimethyl-5-(2,3-dihydroxypropyl)pyrrolidine, reduced with red P and HI followed by Zn and HCl to 2,2-dimethyl-5-propylpyrrolidine (picrolonate m. 218.degree.; oxalate m. 201.degree.), identical with the product of the action of PrMgBr on I followed by redn. Redn. of the product from Me₂CHMgBr and I gave 2,2-dimethyl-5-isopropylpyrrolidine; picrolonate decompd. 245.degree.; oxalate m. 221.degree..

L14 ANSWER 825 OF 825 CA COPYRIGHT 2003 ACS

AN 54:2159 CA

OREF 54:485c-i,486a-i,487a-e

TI Experiments towards the synthesis of corrins. II. Preparation and reactions of 1-pyrroline 1-oxides

AU Bonnett, R.; Brown, R. F. C.; Clark, V. M.; Sutherland, I. O.; Todd, Alexander

CS Univ. Cambridge, UK

SO J. Chem. Soc. (1959) 2094-2102

DT Journal

LA Unavailable

AB cf. C.A. 53, 20036h. The reduction of .gamma.-nitro carbonyl compds. to give 1-pyrroline 1-oxides was described and the reactions of several such N-oxides reported. 4,4-Dimethyl-5-nitro-2-pentanone (33 g.) and 9 g. NH₄Cl in 250 ml. H₂O stirred 2 hrs. with addn. of 45 g. Zn dust, stirring continued a further 2 hrs., the mixt. filtered, the filtrate and washings evapd., the sirup dissolved in 75 ml. CHCl₃, and the CHCl₃ distd. gave 19.8 g. 2,4,4-trimethyl-1-pyrroline 1-oxide(I), hygroscopic oil, b_{0.4} 72.degree., .nu. 1613 cm.⁻¹ .lambda. 229 m.mu., .epsilon. 9000; picrate m. 111.degree. (alc.). MeI deriv., prisms, m. 106.degree. (decompn.) (alc.-Et₂O). Freshly distd. MeCH:CHCHO (17.5 g.) in 25 ml. anhyd. MeOH added dropwise to 25 g. 2-O₂NCHMe₂ in 40 ml. MeOH contg. NaOMe from 1 g. Na at 60.degree., stirred 3 hrs., left overnight, 3 ml. AcOH added, the MeOH evapd., the residue poured into H₂O, the product extd. with Et₂O, the ext. evapd., and distd. gave 20.4 g. 3,4-dimethyl-4-nitropentanal (II), b_{0.6} 80.degree.; semicarbazone, leaflets, m. 150-1.degree. (aq. alc.). Reduction of 60 g. II with 74 g. Zn dust and 15 g. NH₄Cl in 400 ml. H₂O gave 24.3 g. 4,5,5-trimethyl-1-pyrroline 1-oxide (III), b₁ 85.degree., .lambda. 234 m.mu., .epsilon. 8800, .nu. 1572 cm.⁻¹; picrate, lemon yellow laths, m. 112.degree. (alc.). 2-(3-Methyl-3-nitrobutyl)-1,3-dioxolane (50 g.) and 15 g. NH₄Cl in 300 ml. H₂O at 10.degree. treated during 20 min. with 70 g. Zn dust, the mixt. stirred 15 min., filtered, the combined filtrate and washings acidified, left overnight, heated 1 hr. at 75.degree., evapd. to 150 ml., made alk., reduced to 100 ml., after satn. with borax, the soln. extd. with CHCl₃, dried, and fractionated gave 23.6 g. 5,5-dimethyl-1-pyrroline 1-oxide (IV), b_{0.6} 66-7.degree., .lambda. 234 m.mu., .epsilon. 7700, .nu. 1573 cm.⁻¹; picrate, yellow needles, m. 81.degree.. Reduction of 4-methyl-4-nitropentanal with Zn dust and NH₄Cl gave 27% IV and a high boiling residue. 3-(3,4-Methylenedioxyphenyl)-4-nitro-1-phenylbutan-1-one (3.13 g.) and 0.50 g. NH₄Cl similarly treated with Zn in tetrahydrofuran and the product isolated as above gave 1.12 g. 4-(3,4-methylenedioxyphenyl)-2-phenyl-1-pyrroline 1-oxide (V), m. 145.degree. (CH₂Cl₂-Et₂O), .nu. 1613 cm.⁻¹ Reduction of 300 mg. V with 1.2 g. Zn dust and 0.3 g. NH₄Cl in 30 ml. 60% aq. MeOH 8 hrs. at room temp. gave 4-(3,4-methylenedioxyphenyl)-2-phenyl-1-pyrroline, isolated at the HCl salt (200 mg.), m. 235-40.degree. (decompn.). CH₂:CHCHO (14 ml.) added to 36 g. Et .alpha.-nitropropionate in 200 ml. alc. contg. NaOEt (from 0.3 g. Na), the mixt. kept 3 hrs. at 40-50.degree., 1 ml. AcOH added, the solvent evapd., the product extd. with C₆H₆, and distd. gave 31.5 g. Et 2-methyl-2-nitro-5-oxopentanoate (VI), b_{0.5} 107.degree.; 2,4-dinitrophenylhydrazone, orange needles, m. 75-6.degree. (alc.). VI and (CH₂OH)₂ in the presence of p-MeC₆H₄SO₃H gave 78% of the 1,3-dioxolane (VII), b_{0.5} 121-5.degree.. VII (28.5 g.) reduced with 41.5 g. Zn dust in 200 ml. 50% aq. alc. contg. 5.5 g. NH₄Cl, the soln. concd., extd. with CHCl₃, and the soln. evapd. gave 26 g. crude hydroxylamine, b_{0.3} 140-55.degree., viscous oil. The hydroxylamine (25.5 g.) in 400 ml. 0.3N HCl left overnight at room temp., neutralized with NH₄OH, evapd. below 60.degree., the residue extd. with CHCl₃, and fractionated gave 11.6 g. 5-ethoxycarbonyl-5-methyl-1-pyrroline 1-oxide (VIII), b_{0.3} 120.degree.. Treatment of 2.13 g. VIII 1 hr. at 100.degree. with 20 ml. 2.5% NaOH, passage of the soln. through Dowex 50 (H form), and evapn. of the acidic eluate gave 1.37 g. 5-carboxy-5-methyl-1-pyrroline 1-oxide (VIIIa), m. 135-6.degree. (decompn.) (CHCl₃), .lambda. 235-236 m.mu., .epsilon. 7700. KBH₄ (0.4 g.) and 2.5 g. I in 10 ml. H₂O kept 2 days at room temp., satd. with K₂CO₃, extd. with Et₂O, the ext. evapd., and the residue fractionated gave 0.86 g. of the hydroxylamine (IX), b₂₅ 95-100.degree.; H oxalate m. 88.degree. (Me₂CO-Et₂O). Both IX and the salt readily reduced aq. alk. triphenyltetrazolium chloride (IXa) to the red formazan. IX (0.5 g.) in 10 ml. H₂O contg. 1 ml. NH₄OH and 5 mg. CuSO₄ was reoxidized during 2 hrs. to I by passing air through the soln. III (0.63 g.) reduced as above with KBH₄ in H₂O and the cyclic hydroxylamine isolated gave the crude base; addn. of alc. HCl gave 1-hydroxy-2,2,3-triphenylpyrrolidine-HCl, prisms, m. 163.degree. (alc.-Et₂O). Titration in aq. soln. indicated pK_a 5.9. The base readily reduced IXa. I (0.5 g.), 5 g. Zn dust, 2 ml. AcOH, and 8

ml. H₂O refluxed 5 hrs., 2 ml. more AcOH added, heating continued a further 20 hrs., the soln. made alk., and steam distd. gave with picric acid 0.88 g. 2,4,4-trimethyl-1-pyrrolinium picrate (X), m. 192-3.degree. (alc.). I 12 hrs. at room temp. in CHCl₃ satd. with SO₂ gave 15% X. I (0.5 g.), 4 g. granular Sn, 5 ml. concd. HCl, and 5 ml. H₂O refluxed 20 hrs. and worked up as usual gave 0.13 g. X. The mother liquors afforded 0.32 g. 2,4,4-trimethylpyrrolidinium picrate, m. 162.degree..

1-Hydroxy-2,4,4-trimethylpyrrolidine (0.63 g.) and 0.92 g. p-MeC₆H₄SO₂Cl in 10 ml. Et₂O treated with 0.98 g. NEt₃ in 5 ml. Et₂O gave when left overnight at room temp. 1.7 g. triethylammonium salts; the filtrate extd. with dil. HCl, the acid ext. made alk., satd. with K₂CO₃, extd. with Et₂O, and gas chromatographed indicated that the amine product was 2,4,4-trimethyl-1-pyrroline, identified as X (33% yield).

1-Hydroxy-2,2,3-trimethylpyrrolidine (1.1 g.) and 1.55 g. p-MeC₆H₄SO₂Cl in 15 ml. Et₂O treated overnight with 1.64 g. NEt₃ in 5 ml. Et₂O gave an ethereal soln. of the crude bases. These transferred to H₂O by dil. H₂SO₄ and the aq. soln. placed on a column of Amberlite IRC-50 gave 1.08 g. 4,5,5-trimethyl-1-pyrrolinium picrate, prisms, m. 172.degree. (Me₂CO-Et₂O). IV (5 g.) and 3.9 g. KCN in 20 ml. H₂O treated during 1.5 hrs. at 0.degree. with 25 ml. 2N HCl, after a further 2 hrs. the mixt. brought to pH 11, and extd. gave 4.8 g. 2-cyano-1-hydroxy-5,5-dimethylpyrrolidine (XI), prisms, m. 92.degree. (Et₂O-ligroine), .nu. 3230 and 2240 cm.⁻¹ XI (8.1 g.) and 1.5 g. Cu(OAc)₂ in 100 ml. 60% aq. alc. contg. 5 ml. NH₄OH aerated until a blue color was restored, concd. to 30 ml., extd. with CHCl₃, and fractionated gave 5.8 g. 2-cyano-5,5-dimethyl-1-pyrroline 1-oxide (XII), b_{0.5} 110.degree., .nu. 2220 and 1540 cm.⁻¹, .lambda. 271 m.mu., .epsilon. 10,700. III with HCl and KCN as above gave 66% 2-cyano-1-hydroxy-4,5,5-trimethylpyrrolidine (XIII), m. 109.degree. (Et₂O-ligroine), .nu. 3360, 3290, 2270, and 2240 cm.⁻¹ Cu catalyzed air oxidn. of XIII gave 76% 2-cyano-4,5,5-trimethyl-1-pyrroline 1-oxide (XIV), plates, m. 86-7.degree. (EtOAc-ligroine), .nu. 2210 and 1528 cm.⁻¹, .lambda. 273 m.mu., .epsilon. 11,100. VIIIA (0.80 g.) and 0.37 g. KCN in 10 ml. H₂O left 6 hrs. at room temp., the soln. passed through a column of Dowex 50 resin, and the acidic eluate evapd. gave 0.75 g. 5-cyano-1-hydroxy-2-methylpyrrolidine-2-carboxylic acid, m. 133-4.degree. (decompn.) (EtOAc), pKa 3.6, .nu. 3250, 2245, and 1698 cm.⁻¹

2,4,4-Trimethyl-1-pyrroline 1-oxide was recovered in 52% yield after attempted addn. of HCN under the above conditions. XIV (4.1 g.) in 40 ml. 10% aq. NaOH refluxed 3 hrs., the soln. neutralized, and extd. with CHCl₃ gave 1.1 g. 1-hydroxy-4,5,5-trimethyl-2-pyrrolidone, needles, m. 101-2.degree. (Et₂O-ligroine), .nu. 3310, 3120, and 1680 cm.⁻¹, pKa 8.85, deep reddish purple color with FeCl₃. The original aq. soln. adjusted to pH 1 and extd. with CHCl₃ gave 2.4 g. 2-carboxy-4,5,5-trimethyl-1-pyrroline 1-oxide (XIVa), m. 40-1.degree. (C₆H₆), .lambda. 266 m.mu., .epsilon. 8200, pKa 2.85. XII (5 g.) hydrolyzed as above, acidified to pH 1, and extd. with CHCl₃ gave 3.1 g. 2-carboxy-5,5-dimethyl-1-pyrroline 1-oxide (XIVb), m. 86.degree. (Et₂O-ligroine), pKa 2.80, .lambda. 265 m.mu., .epsilon. 8600. The mother liquor from the above crystn. evapd. and an aq. soln. passed down a column of Dowex 50 resin gave 1 g. 1-hydroxy-5,5-dimethyl-2-pyrrolidone (XV), m. 82-3.degree. (hexane), pKa 8.7, .nu. 3320, 3090, and 1678 cm.⁻¹ An authentic sample of XV prepd. by reduction of 21 g. Me 4-methyl-4-nitropentanoate with 30 g. Zn dust and 6 g. NH₄Cl in 50% aq. alc., the mixt. stirred 4 hrs., the solids removed, the filtrate evapd. to a sirup, this sirup in 50 ml. 2N HCl extd. with CHCl₃, and evapd. gave 4.8 g. XV. XIVa (100 mg.) was heated 3 min. at 140-50.degree. (CO₂ evolved), and the oily residue converted into the picrate, identified as 120 mg. III picrate. XIVb treated as above gave XII, isolated as the picrate, m. 78-9.degree.. XII (10 g.) in 30 ml. Et₂O refluxed 0.5 hr. with EtMgBr (from 15 g. EtBr and 3.4 g. Mg), excess aq. NH₄Cl added, the Et₂O layer sepd., dried, and fractionated gave 11.2 g. 5-ethyl-1-hydroxy-2,2-dimethylpyrrolidine (XVI), b_{0.7} 50-3.degree.. Air oxidn. of XVI in aq. alc. contg. Cu(OAc)₂ and NH₄OH gave 90% corresponding nitron, b_{0.2} 54-6.degree., .nu. 1600 cm.⁻¹; picrate, yellow needles, m. 71-2.degree. (alc.). XII (2 g.) treated as above with MeMgI followed by

Cu catalyzed air oxidn. of the intermediary hydroxylamine and treatment with picric acid gave 1.9 g. 2,5,5-trimethyl-1-pyrroline 1-oxide picrate, m. 98.degree.(alc.). I (10 g.) treated with MeMgI gave 9 g. 1-hydroxy-2,2,4,4-tetramethylpyrrolidine (XVII), sublimed at 75.degree./14 mm., m. 62.degree.. Cu catalyzed air oxidation of 8.5 g. XVII gave 72% 3,3,5,5-tetramethyl-1-pyrroline 1-oxide, b1 73.degree., m. 32-4.degree. (ligroine); picrate m. 137-8.degree.(alc.). MeNO2 (11.7 g.) in 50 ml. alc. left at room temp. overnight with 10.5 g. IV and 1.8 g. Na in 200 ml. alc., acidified, and evapd. gave 11.8 g. 1-hydroxy-2,2-dimethyl-5-nitromethylpyrrolidine, yellow oil, b0.3 98.degree., .nu. 3220 and 1552 cm.-1. Similarly, 12.6 g. EtNO2 added to 9.5 g. IV gave 3.7 g. 1-hydroxy-2,2-dimethyl-5-(1-nitroethyl)pyrrolidine, b0.4 100-2.degree., .nu. 3480 and 1548 cm.-1; 5.7 g. IV was recovered. I (0.50 g.), 0.45 g. BzH, and 50 mg. KOH in 4 ml. alc. refluxed 0.5 hr., poured into H2O, and crystd. gave 0.31 g. 4,4-dimethyl-2-styryl-1-pyrroline 1-oxide, m. 113.degree. (C6H6-ligroine), .nu. 1537, 990, 977, 756, and 691 cm.-1, .lambda. 236 and 329 m.mu., .epsilon. 11,200 and 22,600. A similar condensation with p-O2NC6H4CHO gave 4,4-dimethyl-2-(4-nitrostyryl)-1-pyrroline 1-oxide, leaflets, m. 233.degree. (alc.). I (0.4 g.) benzoylated and the crude material passed through Al2O3 and concd. gave 0.51 g. 5-benzamido-1-benzoyloxy-4,4-dimethylpentan-2-one (XVIII), prisms, m. 117.degree. (80% MeOH), .nu. 3360, 1718, 1637, and 1547 cm.-1, .lambda. 231 and 270 m.mu., .epsilon. 25,700 and 1800. Hydrolysis of XVIII (113 mg.) with aq. alc. KOH gave 67 mg. BzOH; 2,4-dinitrophenylhydrazone, prisms, m. 172.degree. (alc.), .lambda. 356-8 m.mu., .epsilon. 21,900.

=> d his

(FILE 'HOME' ENTERED AT 11:11:52 ON 03 MAY 2003)

FILE 'REGISTRY' ENTERED AT 11:12:06 ON 03 MAY 2003

```

      E 66893-81-0/CN
      E POBN/CN
L1      1 S E3
      E 66893-81-0/RN
L2      1 S E3
      E 3376-24-7/RN
L3      1 S E3
      E 3317-61-1/RN
L4      1 S E3
      E 2564-83-2/RN
L5      1 S E3

```

FILE 'REGISTRY' ENTERED AT 11:15:40 ON 03 MAY 2003

```

      SET TERMSET E#
      DEL SEL Y
      SEL L1 1 RN
L6      1 S E1/RN
      SET TERMSET LOGIN

```

FILE 'CHEMLIST' ENTERED AT 11:15:45 ON 03 MAY 2003

```

L7      1 S L6

```

FILE 'CA' ENTERED AT 11:20:02 ON 03 MAY 2003

```

L8      144 S L1
L9      144 S L2
L10     1014 S L3
L11     144 S L2
L12     144 S L1
L13     1014 S L3
L14     825 S L4

```

=> s 15

L15 2379 L5

=> d l15 2374-2379 bib,ab

L15 ANSWER 2374 OF 2379 CA COPYRIGHT 2003 ACS

AN 61:54445 CA

OREF 61:9381h,9382a-b

TI Nitroxides. VI. Stable piperidine and pyrrolidine free radicals. Effects of solvents on the ultraviolet and electron paramagnetic resonance spectra. Conformational mobility of radicals

AU Briere, R.; Lemaire, H.; Rassat, A.

CS C. E. N., Grenoble, Fr.

SO Tetrahedron Letters (1964), (27-28), 1775-80

DT Journal

LA French

AB An essential property of the nitroxides I (R = O; H, OH; H₂; :NOH; Me, OH) (II, III, IV, V, VI) and VII is the nonbasic character, which permits their sepn. from the starting amine by washing with acid. The nonbasicity indicates a participation of the N free pair in a 3-electron N-O linkage and a shielding of the unpaired electron of O from external attack, thus contributing to the stability of the radicals. The radicals showed ultraviolet (UV) absorption bands at λ . 405-450 m. μ . (ϵ . 24,700-22,222) sensible to solvent effect, decreasing from nonpolar to polar solvents, and a 2nd band around λ . 240 m. μ . (ϵ . 3000). As a 1st approximation, the nitroxide group can be described as a ketyl group, a carbonyl with an electron fixed in the 1st antibonding level π^* . The behavior of the band at 450 m. μ ., varying with the solvent, is characteristic of a forbidden transition $\pi \rightarrow \pi^*$ by reasons of symmetry. The frequencies of max. absorption varies linearly with the Kosower Z factor. Similarly, the variation of aN, the hyperfine splitting of N found in electron spin resonance (e.s.r.), on change of solvent is related to the factor Z and not to the dielec. const. of the medium. Although I and VII have closely related structures, the e.s.r. spectra permit observation of various characteristics related to the structure, in particular the variation of aN with the solvent and with the structure, and in compds. II, V, and VI the variation of a13c with the structure.

L15 ANSWER 2375 OF 2379 CA COPYRIGHT 2003 ACS

AN 60:52651 CA

OREF 60:9240c-h

TI Organic radical reactions involving no free valence

AU Rozantsev, E. G.; Neiman, M. B.

CS Inst. Chem.-Phys., Acad. Sci. U.S.S.R., Moscow

SO Tetrahedron (1964), 20(1), 131-7

DT Journal

LA Unavailable

AB A radical, possessing a reactive group together with the free valence, might react in 2 ways and an attempt was made to direct the chem. process through the reactive group by increasing the steric hindrance close to the atom carrying the free valence, thus leaving aside the unpaired electron. The previously unobserved heterocyclic free radical, 2,2,6,6-tetramethyl-4-piperidone nitrogen oxide (I), was synthesized as a structural model. Ag₂O (0.02 g.-mole) and 0.01 g.-mole 2,2,6,6-tetramethyl-4-piperidone hydroxide refluxed 1 hr. in 25 ml. dry Et₂O yielded 74.7% I, m. 36.degree., 5.9 .times. 10²³ spins/mole. The high kinetic stability and the electron spin resonance (e.s.r.) spectrum of I were discussed. I (0.01 g.-mole) in 5 ml. MeOH added to 0.01 g.-mole HONH₂ in 5 ml. MeOH yielded 51% I oxime, m. 180.degree., 6.0 .times. 10²³ spins/mole. I (0.01 g.-mole) in H₂O poured into satd. aq. H₂NNHCONH₂.HCl, and excess concd. aq. K₂CO₃ added gave the semicarbazone, m. 215.degree. (decompn.) (abs. alc.), with e.s.r. spectrum similar to that of I. I similarly gave a 2,4-dinitrophenylhydrazone, m. 250.degree. (decompn.), e.s.r. spectrum similar to that of I. I catalytically reduced with PtO₂, Pd-C, or Raney Ni gave a substituted diamagnetic hydroxylamine, also obtained according

to Lehmann (Ber. 30, 2736(1897)) from phorone and H₂NOH. The specific reactivity of the ketone group was particularly evident from the ready rearrangement of I with excess HONH₂.HCl. Satd. aq. I (1.7 g.) treated at 20.degree. with 0.76 g. HONH₂.HCl in a min. of H₂O yielded 30% 2,2,7,7-tetramethyl-5-homopiperazinone (Ia) nitrogen oxide (II), m. 162.degree. (Et₂O), 5.8 .times. 10²³ spins/mole. Catalytic amts. of trylon-B and Na₂WO₄.2H₂O in 5 ml. H₂O and 3 ml. 30% H₂O₂ added to 3.4 g. Ia (m. 147-8.degree.) in 3 ml. warm MeOH and the mixt. kept 16 hrs. yielded 70% II. II is a rose-colored cryst. paramagnetic compd. with 2 possible conformational isomers. I (0.3 g.-mole) in 100 ml. dry Et₂O added slowly to EtMgBr (24 g. Mg, 109 g. EtBr) in 220 ml. dry Et₂O, the mixt. refluxed gently 4 hrs. (H₂O-free conditions), and kept 16 hrs. gave 48 g. I and 2,2,6,6-tetramethyl-4-ethyl-4-piperidinol (IIa) nitrogen oxide (III). Na₂WO₄.2H₂O (15 mg.), 20 mg. trylon-B, 4 ml. H₂O, and 2 ml. 30% H₂O₂ added to 1.85 g. IIa (m. 66.degree.) in 4 ml. H₂O, the mixt. kept 24 hrs. at 20.degree., satd. with solid K₂CO₃, extd. with Et₂O, and the product submitted to thin-layer chromatography on Al₂O₃ in 1:1 MeOH-Me₂CO gave the same chromatographic const. as that of III. The paramagnetic redn. product of the oxo group was obtained by decompn. of the hydrazone radical by the Kizhner method (Rozantsev, et al., CA 58, 10165e). I (0.06 g.-mole), 9.5 g. 85% N₂H₄.H₂O, and 15 g. KOH in 100 g. (HOCH₂CH₂)₂O refluxed 1.5 hrs. at 150.degree., the mixt. distd. into a liquid N-cooled receiver, and the distillate repeatedly extd. with Et₂O yielded 8% 2,2,6,6-tetramethylpiperidine (IIIa) nitrogen oxide (IV), m. 38-9.degree.. Na₂WO₄.2H₂O (15 mg.), 10 mg. trylon-B, and 1.5 ml. 30% H₂O₂ in 5 ml. H₂O added to 70 g. IIIa in 5 ml. MeOH and the mixt. kept 2 days yielded 70.5% IV. The extremely high volatility and strongly camphor-like smell may be accounted for by the globular stereometry of IV.

L15 ANSWER 2376 OF 2379 CA COPYRIGHT 2003 ACS

AN 60:26203 CA

OREF 60:4661g-h,4662a-b

TI Ganglioplegic activity of di-tert-butyl nitroxide, a stable free radical, and analog

AU Cummings, J. R.; Grace, J. L.; Latimer, C. N.

CS Am. Cyanamide Co., Pearl River, NY

SO J. Pharmacol. Exptl. Therap. (1963), 141(3), 349-55

DT Journal

LA Unavailable

AB Oral and intravenous hypotensive activities of di-tert-butyl nitroxide (tert-Bu₂NR: R = O) (I) and 15 analogs were studied in rats, dogs, and cats. Nine of the compds. tested lowered the blood pressure and also significantly augmented the vasopressor responses to intravenous epinephrine and phenylethylamine. An immediate hypotensive response was evoked by the free radicals I and 2,2,6,6-tetramethylpiperidine N-oxide and by the corresponding hydroxy hydrochlorides, showing that the presence of the free electron did not confer unusual pharmacol. activity. Bladder contractions to stimulation of the preganglionic pelvic nerve fibers were blocked by I intraarterially and, in smaller doses, intravenously. I also blocked contractions elicited by intraarterial dimethylphenylpiperazinium but the increased tone produced by intraarterial serotonin was either unaffected or augmented. A similar effect was produced by II (R = OH). The increases in heart rate and contractile force produced by preganglionic stimulation of stellate cardiac nerve were blocked by I but the same effects resulting from postganglionic stimulation were unaffected. Enhanced salivary flow induced by pilocarpine was unaltered by I. The normal postganglionic potentials produced by stimulation of preganglionic fibers of the superior cervical sympathetic nerve in cats were blocked by both I and II, as were the contractions of the nictitating membrane. The effects of postganglionic stimulation were unaffected. Acute toxicities of I and II (L.D.₅₀, mg./kg., oral and intravenous) were I, 505, 53.8 and II, 222, 49.7. Dogs given 20 times the ganglioplegic dose orally showed symptoms due to ganglionic blockade (mydriasis, loss of accomodation, and nictitating membrane relaxation) but no deaths.

L15 ANSWER 2377 OF 2379 CA COPYRIGHT 2003 ACS

AN 59:66851 CA

OREF 59:12330b-c

TI Nature of the spin-lattice interaction in magnetically diluted free radicals

AU Il'yasov, A. V.; Garif'yanov, N. S.; Timerov, R. Kh.

CS Phys.-Tech. Inst., Kazan Branch Acad. Sci. U.S.S.R., Kazan

SO Dokl. Akad. Nauk SSSR (1963), 150(3), 588-91

DT Journal

LA Unavailable

AB The electron paramagnetic resonance was studied for solid (supercooled) solns. of the free radicals of .alpha.,.alpha.-diphenyl-.beta.-picrylhydrazyl and of 2,2,6,6-tetramethylpiperidine oxide in EtOH, MeOH, C₆H₆, PhMe, and in mixts. of the alc. with glycerol and with H₂O. The results show that the time for spin-lattice relaxation in the supercooled solns. with a radical concn. of 10-210-3M is independent of concn. and the nature of the solvent. The mechanism for the spin-lattice interaction is greatly dependent on the type of solvent.

L15 ANSWER 2378 OF 2379 CA COPYRIGHT 2003 ACS

AN 59:6672 CA

OREF 59:1204f-g

TI Electron spin resonance (E.S.R.) in liquid and supercooled solutions of some free radicals

AU Garif'yanov, N. S.; Il'yasov, A. V.; Yablokov, Yu. V.

CS Phys. Tech. Inst. Branch Acad. Sci., U.S.S.R., Kazan

SO Dokl. Akad. Nauk SSSR (1963), 149, 876-9

DT Journal

LA Unavailable

AB The effect of the immediate environment of the mol. spin on the parameters of the hyperfine structure of .alpha.,.alpha.-diphenyl-.beta.-picrylhydrazyl and of 2,2,6,6-tetramethylpentamethylene N oxide was studied. The measurements were made at 9320 Mc. in the temp. range 77-300.degree.K. MeOH, EtOH, glycerol-MeOH mixt., C₆H₆, toluene, CHCl₃, and polystyrene dild. with C₆H₆ or CHCl₃ were used as solvents. Equations are derived for describing the E.S.R. spectrum in liquid and supercooled solns. A table of the parameters of the hyperfine structure shows that the ratio of the consts. of the isotropic hyperfine structure depends noticeably on the solvent. Measurement of the g factor of tetramethylpentamethylene N oxide at 36,000 Mc. showed that the anisotropy was not more than 0.002.

L15 ANSWER 2379 OF 2379 CA COPYRIGHT 2003 ACS

AN 58:44164 CA

OREF 58:7523d-e

TI Effect of solvents on the electron paramagnetic resonance (E.P.R.) spectra of some free radicals

AU Il'yasov, A. V.

SO Zh. Strukt. Khim. (1962), 3, 95-7

DT Journal

LA Unavailable

AB The effect of solvents on the E.P.R. spectra of the free radicals I and II was studied at a frequency of 9320 Mc. The width of the line, .delta.H, was measured as the distance between the max. and min. of the first deriv. of the absorption curve. I had .delta.H and sepn. of the components as follows: in C₆H₆, PhMe, and CHCl₃, 7 and 15.6 oe.; in EtOH, 6.4 and 16.8 oe.; in 40% aq. EtOH, 4.4 and 18.9 oe. Similarly for II .delta.H and the sepn. were, resp.; in C₆H₆, PhMe, and CHCl₃, 6 and 11.7 oe.; and in EtOH + 30% H₂O, 4 and 13 oe. The difference in .delta.H for the aq. solns. is not due to viscosity, because heating to 40.degree. to equalize the viscosities does not remove the difference. The phenomenon may be caused by the presence of a solvation shell around the free radicals.

=> d 111 139-144 bib,ab

L11 ANSWER 139 OF 144 CA COPYRIGHT 2003 ACS

AN 92:102211 CA

TI Photolysis of alkylcobaloximes, methylsalen, cobalamines and coenzyme B12 in protic solvents: an ESR and spin-trapping technique study

AU Maillard, Ph.; Giannotti, C.

CS Inst. Chim. Subst. Nat., CNRS, Gif sur Yvette, 91190, Fr.

SO Journal of Organometallic Chemistry (1979), 182(2), 225-37

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

AB The photolysis in protic solvents in the visible region >420 nm of several alkylcobaloximes, cobalamines, methylsalen, and coenzyme B12 was studied by ESR spectroscopy including the use of spin-trapping techniques involving 5,5'-dimethylpyrroline-N-oxide (DMPO), ~~phenyl N-tert-butyl~~ nitron, and .alpha.-4-pyridyl-1-oxide-N-tert-butyl nitron. During the photolysis, H atoms are probably abstracted from the C(10) position of the corrin equatorial ligand in the case of coenzyme B12 and cobalamine derivs. The ESR spectra of the anaerobic photolysis of alkylcobaloximes in aprotic solvents in the presence of DMPO, followed by the addn. of air or pure O, provide evidence for intraligand radical spin-trapping reactions.

L11 ANSWER 140 OF 144 CA COPYRIGHT 2003 ACS

AN 92:31909 CA

TI Spin trapping and electron spin resonance detection of radical intermediates in the photodecomposition of water at titanium dioxide particulate systems

AU Jaeger, Calvin D.; Bard, Allen J.

CS Dep. Chem., Univ. Texas, Austin, TX, 78712, USA

SO Journal of Physical Chemistry (1979), 83(24), 3146-52

CODEN: JPCHAX; ISSN: 0022-3654

DT Journal

LA English

AB Spin trapping and ESR detection [with the traps .alpha.-Ph N-tert-Bu nitron and .alpha.-(4-pyridyl N-oxide) N-tert-Bu nitron] were used to detect free-radical intermediates formed during in situ irradiation of TiO2 and platinized TiO2 powders in aq. solns. Evidence for the production of OH radical (formed in the oxidation of H2O) and HO2 radical (probably formed in a reduction step) is presented. Other spin adducts, attributed to decomposition reactions of the spin traps, were also found. The results suggest an important role for photogenerated OH in many photocatalytic and photosynthetic processes using TiO2 powders.

L11 ANSWER 141 OF 144 CA COPYRIGHT 2003 ACS

AN 92:2794 CA

TI Spin trapping of superoxide

AU Finkelstein, Eli; Rosen, Gerald M.; Rauckman, Elmer J.; Paxton, John

CS Med. Cent., Duke Univ., Durham, NC, 27710, USA

SO Molecular Pharmacology (1979), 16(2), 676-85

CODEN: MOPMA3; ISSN: 0026-895X

DT Journal

LA English

AB Due to conflicting reports in the literature, the spin trapping of superoxide by the nitron 5,5-dimethyl-1-pyrroline N-oxide (I) was reinvestigated. Superoxide could indeed be trapped and the 5,5-dimethyl-2-hydroxylpyrrolidinoxyl (II) and 5,5-dimethyl-2-hydroperoxypyrrolidinoxyl (III) adducts were distinguishable. In contrast to earlier work, III was highly unstable and decomposed into II. 2,5,5-Trimethyl-1-pyrroline N-oxide (TMPO), a spin trap structurally similar to I but lacking a .beta.-hydrogen, formed a stable nitroxide upon reaction with superoxide. Rate constants for the reaction of superoxide

with I and TMPO were measured and indicated that spin trapping was an extremely inefficient method for the detection of superoxide. The new spin trap, .alpha.-4-pyridyl-1-oxide-N-tert-butyl nitron (POBN), was also capable of distinguishing the difference between superoxide and hydroxyl radical. The nitroxide formed upon the reaction of superoxide with POBN was unstable.

L11 ANSWER 142 OF 144 CA COPYRIGHT 2003 ACS

AN 91:108398 CA

TI The ESR spin trapping chemistry of .alpha.-(4-pyridyl 1-oxide) N-tert-butyl nitron and poly(phenyl-N-tert-butyl nitron)

AU Wang, Yeeyang

CS Univ. Georgia, Athens, GA, USA

SO (1978) 194 pp. Avail.: Univ. Microfilms Int., Order No. 7914065

From: Diss. Abstr. Int. B 1979, 39(12, Pt. 1), 5961

DT Dissertation

LA English

AB Unavailable

L11 ANSWER 143 OF 144 CA COPYRIGHT 2003 ACS

AN 90:5442 CA

TI On spin trapping hydroxyl and hydroperoxy radicals

AU Janzen, Edward G.; Nutter, Dale E., Jr.; Davis, Edward R.; Blackburn, Barry J.; Poyer, J. Lee; McCay, Paul B.

CS Guelph-Waterloo Cent. Grad. Work Chem., Univ. Guelph, Guelph, ON, Can.

SO Canadian Journal of Chemistry (1978), 56(17), 2237-42

CODEN: CJCHAG; ISSN: 0008-4042

DT Journal

LA English

AB The assignments of the HO.bul., HOO.bul., and ROO.bul. (R = alkyl) radical spin adducts of PhCH:N+(O-)CMe3 are discussed. Results of new expts. designed to test the assignments of the first two are described. The HO.bul. adduct assignment is correct. The relation between a.beta.Hand aN is detd. and gives a good fit for the 7 pairs of consts. reported for the HO.bul. adduct. The assignments for the HOO.bul. adduct may be correct but no proof is available.

L11 ANSWER 144 OF 144 CA COPYRIGHT 2003 ACS

AN 89:23427 CA

TI Spin trapping with .alpha.-pyridyl 1-oxide N-tert-butyl nitrones in aqueous solutions. A unique electron spin resonance spectrum for the hydroxyl radical adduct

AU Janzen, Edward G.; Wang, Y. Y.; Shetty, Raghav V.

CS Guelph Waterloo Cent. Grad. Work Chem., Univ. Guelph, Guelph, ON, Can.

SO Journal of the American Chemical Society (1978), 100(9), 2923-5

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB The spin-trapping chem. of .alpha.-4-pyridyl 1-oxide N-tert-Bu nitrones is described in aq. soln. as applied to the problem of detecting HO.bul. radical. Hyperfine-splitting consts. of the hydroxyl adduct are shown as a function of pH and H2O2 concn. A 2nd set of doublets was obsd. which were attributed to a 2nd nitroxide; this may be the hydroperoxy adduct, but this assignment is unsupported at this time.

=> s 13

L13 1014 L3

=> d his

(FILE 'HOME' ENTERED AT 11:11:52 ON 03 MAY 2003)

FILE 'REGISTRY' ENTERED AT 11:12:06 ON 03 MAY 2003